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Survey of Chloroform Emission Sources

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Survey of Chloroform Emission Sources

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The potential public health impact of chloroform exposure is being investigated. This document contains information onthe sources of chloroform emissions, current emission levels, control methods that could be used to reduce chloroform emissions, and cost estimates for employing controls.

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Emission Standards and Engineering Division

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Air and Radiation
Office of Air Quality Planning and Standards
Research Triangle Park, NC 27711

October 1985

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1. EXECUTIVE SUMMARY

This source assessment provides information on emissions and potential emission controls for chloroform. Chloroform is one of a number of potential hazardous air pollutants being screened by the U.S. Environmental Protection Agency to determine if regulatory action under the Clean Air Act is warranted. Part of this screening procedure includes development of a source assessment for each chemical. Other portions of the screening procedure include evaluation of health effects data and pollutant exposure data. Based on these and other data, the Administrator will determine if chloroform emissions should be regulated.

Included in this report is information on all significant sources of chloroform identified to date, emissions, current control, achievable control, control costs, and cost-effectiveness.

Eleven source categories are discussed to varying degrees in this report. These are:

- Pulp and paper manufacturing,
- Ethylene dichloride manufacturing,
- Chloroform production,
- Fluorocarbon 22 production,
- Oxybisphenoxarsine manufacturing,
- Pharmaceutical manufacturing,
- Trichloroethylene photodegradation,
- Chlorination of cooling water,
- Chlorination of drinking water,
- Chlorination of municipal wastewater, and
- Grain fumigation.

Emissions data are reported for the eleven source categories listed above and for Hypalon® manufacturing. Production data on Hypalon® manufacturing have been claimed to be confidential and are not included in the body of this report. The source categories listed above emit 8,740 Mg of chloroform annually. Two sources not listed above include laboratory uses and miscellaneous uses. These categories are too disaggregated for reliable emission estimates to be possible. However, assuming all chloroform production attributable to miscellaneous uses ends up as air emissions, an additional 6,000 Mg could be emitted to the atmosphere. This estimate is based on a production level of 159,500 Mg of which 90 percent goes to chlorofluorocarbon 22 production, 5 percent is exported, and approximately 2,000 Mg is used in pharmaceutical manufacturing.

Of the eleven source categories listed above, four form chloroform by the reaction of chlorine with organic precursors in water. Chloroform emissions result from intermedia transfer of chloroform from water to air. These "inadvertent" emissions account for 74 percent of all chloroform emissions (Figure 1-1). Although these emissions are secondary, there are methods to control these releases, the principal method being substitution away from chloroform forming oxidants such as free chlorine or hypochlorite to compounds such as chlorine dioxide or chloramines.

Another secondary source of chloroform in the atmosphere is the photodegradation of trichloroethylene. Control methods for this source would include substitution to other halogenated solvents, or use of other cleaning methods.

Direct sources of chloroform emissions result from chloroform production, its use as a solvent, and its use as an intermediate in the production of other chemicals such as fluorocarbon 22, which uses up to 90 percent of all chloroform produced. Here, conventional control techniques to limit chloroform emissions would apply.

Source categories which emit chloroform by order of decreasing emissions are briefly described below. Included in this discussion are potential controls, costs, and cost-effectiveness.

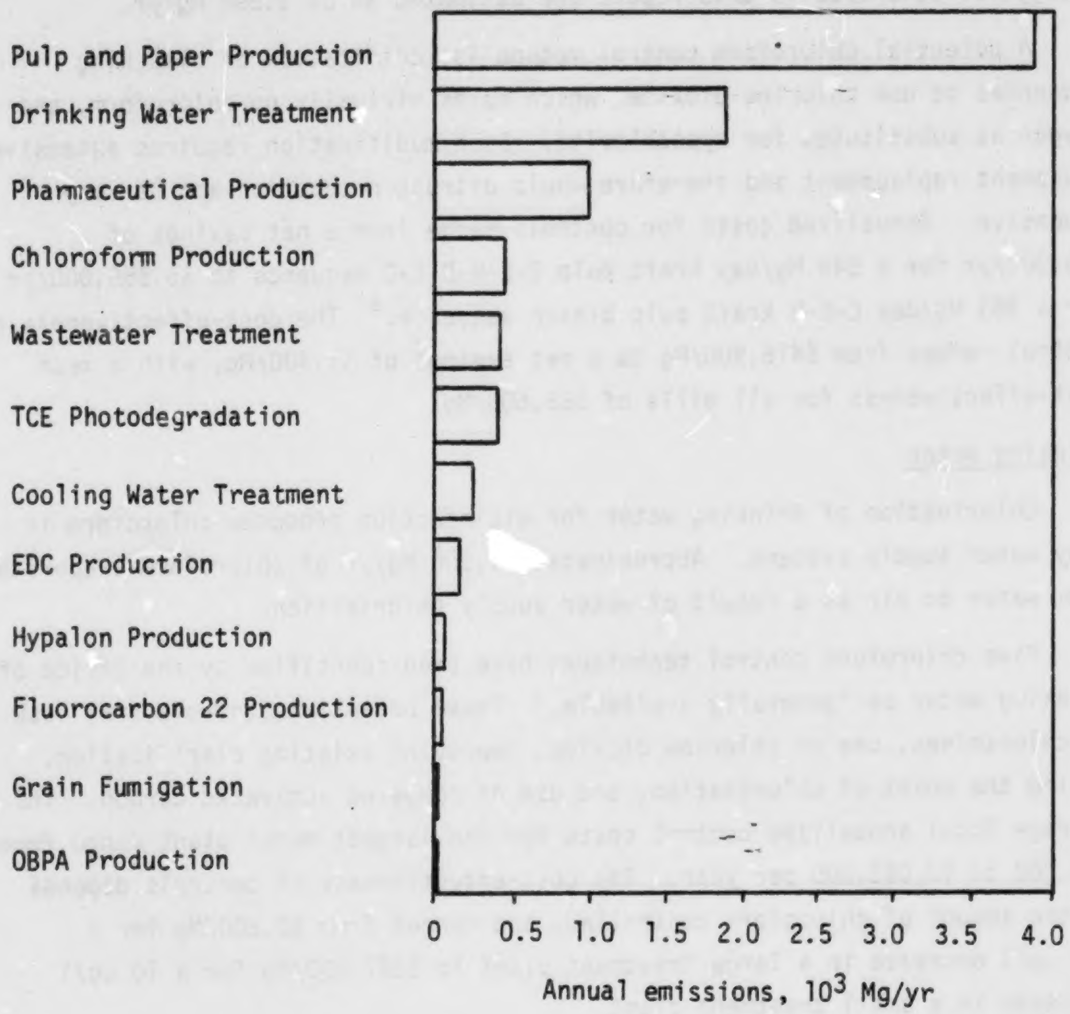

Figure 1-1. Sources of Chloroform Emissions.

Pulp and Paper Industry

Chloroform air emissions result from wastewater treatment facilities at pulp and paper mills where chlorine compounds are used in pulp bleaching. The principal source of chloroform in the pulp and paper industry is the hypochlorite bleaching stage in pulp bleaching sequences (92 percent of chloroform produced in pulp bleaching). Chloroform emissions from the five subcategories described in this report are estimated to be 3,890 Mg/yr.

A potential chloroform control method is modification of bleaching sequences to use chlorine dioxide, which forms virtually no-chloroform, and oxygen as substitutes for hypochlorite. Such modification requires extensive equipment replacement and therefore would disrupt production and be very expensive. Annualized costs for controls range from a net savings of \$25,000/yr for a 545 Mg/day kraft pulp C-E-H-D-E-D sequence to \$5,550,000/yr for a 363 Mg/day C-E-H kraft pulp bleach sequence.[a] The cost-effectiveness of control ranges from \$416,900/Mg to a net savings of \$1,400/Mg, with a mean cost-effectiveness for all mills of \$85,600/Mg.

Drinking Water

Chlorination of drinking water for disinfection produces chloroform in many water supply systems. Approximately 1,900 Mg/yr of chloroform evaporate from water to air as a result of water supply chlorination.

Five chloroform control techniques have been identified by the Office of Drinking Water as "generally available." These potential controls are: use of chloramines, use of chlorine dioxide, improving existing clarification, moving the point of chlorination, and use of powdered activated carbon. The average total annualized control costs for the largest model plant range from \$99,000 to \$3,093,000 per year. The cost-effectiveness of controls depends on the amount of chloroform controlled, and ranged from \$2,800/Mg for a 100 μg/l decrease in a large treatment plant to \$877,000/Mg for a 10 μg/l decrease in a small treatment plant.

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[a] Refer to page 3-5 for an explanation of these symbols

Chloroform Production

There are six chloroform production facilities currently operating in the U.S., with a current estimated chloroform emission total of 458 Mg/yr. Sixty percent of these emissions are from fugitive sources such as fugitive leaks from process components, losses from loading chloroform into transport vessels, and several secondary emission sources. The remaining 40 percent is due mostly to chloroform storage, with significant process vent emissions at a few plants. Available control technology (ACT) could be used to reduce emissions to 144 Mg/yr, mostly by controlling process fugitive sources and storage tanks. After ACT, emissions would consist mostly of remaining process fugitives, uncontrolled secondary emissions and in-process storage not covered by ACT controls on main product storage tanks. For storage, handling, and some plants' process vents, ACT consists of refrigerated condensers. Process fugitive emissions can be controlled by a combination of monthly inspection and maintenance, and additional equipment specifications for some process components.

The total net annual cost for implementation of ACT for chloroform production facilities is estimated at $525,000. About $410,000 of this total is for control of chloroform handling, the most expensive ACT with an average cost-effectiveness of $9,100/Mg. Almost all of the remaining cost is divided between process fugitive controls ($51,000/yr; $380/Mg) and storage controls ($59,000/yr; $630/Mg). The net costs and cost-effectiveness of individual controls varies significantly, due to differences in chloroform recovery credits and the level of controls already in place. Total estimated annual costs per plant vary from $12,300 for a plant with most ACT controls in place, to $135,000 for a plant requiring two separate handling control systems as well as other controls. Cost-effectiveness at the plant level is estimated to range from $960/Mg to $5,800/Mg.

Municipal Wastewater Treatment

It is estimated that 424 Mg of chloroform are generated and released to the environment as a result of wastewater treatment and disinfection. On average, the amount of chloroform in wastewater decreases by 4.6 μg/l from influent to secondary effluent. With 9.2081×10^{10} liters treated per day, national emissions from wastewater treatment are 155 Mg/yr. In addition, chlorination of treated effluent increases chloroform concentrations in wastewater by 8 μg/l. Thus, an additional 269 Mg of chloroform are generated annually as a result of disinfection of effluent.

Methods of control to reduce chloroform formation due to disinfection include precursor removal prior to chlorination (improved clarification), or use of a disinfectant that does not form chloroform (use of chloramines or chlorine dioxide). Control efficiency ranges from 37 to 90 percent depending on the method used. Annualized control costs range from $8,000 for a small plant using chloramines to $1,120,000 for a large plant using improved clarification. Cost-effectiveness ranges from $38,700/Mg for a large plant using chloramines to $1,560,000/Mg for a small plant using improved clarification.

Trichloroethylene Photodegradation

Chloroform forms in the atmosphere as a result of photodecomposition of trichloroethylene. It is estimated that for every ppm of trichloroethylene emitted to the atmosphere, 7 ppb of chloroform are formed. In 1982, 67,200 Mg of trichloroethylene were emitted to the atmosphere, resulting in the formation of 420 Mg of chloroform. Methods of control include use of alternative halogenated solvents for solvent degreasing, or alternative cleaning methods.

Cooling Water

Chloroform is formed when cooling water in steam electric plants is chlorinated to prevent biofouling in heat-exchange equipment. An estimated 197 to 263 Mg/yr of chloroform are produced and emitted from cooling water chlorination.

Potential chloroform control could be attained by using alternative biofouling control methods such as other oxidizing chemicals, nonoxidizing biocides, and mechanical cleaning. None of these alternatives is used widely at this time.

Ethylene Dichloride Production

There are a total of 20 ethylene dichloride production facilities in the U.S. It is estimated that emissions of byproduct chloroform from these facilities are currently about 173 Mg/yr. The main emission sources include oxychlorination reactors, purification and separation columns, and a few reported instances of emissions from liquid waste storage or disposal and other waste-treatment steps. At all but two plants, all reactor and column vents are controlled by thermal oxidation, which has efficiency of 98 percent or greater. Applying a similar level of control to these vents at the two remaining plants is estimated to reduce total chloroform emissions to 117 Mg/yr. The majority of this emission reduction is due to uncontrolled column vents at one plant. Costs and cost-effectiveness were not estimated for the few remaining potential controls due to the high level of existing control in the industry, and unavailability of sufficient plant-specific data.

Fluorocarbon 22 Production

There are currently six facilities in the U.S. that produce fluorocarbon 22 on a routine basis. These facilities are estimated to emit about 50 Mg, almost entirely from storage of chloroform feedstock. With 95 percent control of all storage emissions by refrigerated condensers, this total can be reduced to about 5.7 Mg/yr. This would involve installation of condensers at four plants, at a total net annual cost of $122,300. For individual plants, these controls are estimated to cost from $2,200/Mg to $4,100/Mg, with an industry-wide average of $2,800/Mg.

Oxybisphenoxarsine/1,3-Diisocyanate Manufacture

Oxybisphenoxarsine (OBPA) and 1,3-diisocyanate are both produced by Aerojet General Corporation in Sacramento, California. OBPA is a fungicide which is combined with rubber to prevent mold growth on gaskets and seals. 1,3-Diisocyanate is an intermediary in the production of polyurethane resins.

Combined chloroform emissions from these two processes amount to 23.77 Mg/yr. Both sources are controlled by carbon adsorption. A third source of chloroform emissions is a deaerator of hazardous waste prior to deep well injection. Reported emissions from this source are 25.5 Mg/yr. There are no known controls for this source.

Grain Fumigation

Chloroform has been used as a carrier in grain fumigation. Vulcan Materials Company markets Chlorofume® FC 30 Grain Fumigant containing 72.2 percent chloroform, 20.4 percent carbon disulfide, and 7.4 percent ethylene dibromide. In 1981, 28.4 Mg of chloroform were used in this manner.

Because of the recent cancellation of pesticide products containing EDB (49 FR 4452), it is not known whether Vulcan plans to reformulate Chlorofume® without EDB. If so, a potential substitute to chloroform as a carrier would be carbon tetrachloride, which is used as a carrier in virtually all other fumigants.

Pharmaceutical Manufacture

Specific data on uses of chloroform in the pharmaceutical industry are very limited. A recent survey conducted by the Pharmaceutical Manufacturers Association indicates that total direct air emissions from this source category are on the order of 1000 Mg/yr. This total includes the known use of chloroform as a solvent in production of Vitamin C at one Hoffman-LaRoche plant, where total emissions are estimated at about 220 Mg/yr. Further information is not available on one other very small Vitamin C production facility (Pfizer, Groton, CT), or on other uses of chloroform in pharmaceutical manufacturing.

2. INTRODUCTION

The purpose of this report is to provide information on sources of air emissions of chloroform. Chloroform is one of a number of chemical compounds being screened by the U.S. Environmental Protection Agency to determine whether they should be regulated under the Clean Air Act. Results of this source assessment will be combined with other information, such as health effects data and exposure data, to form a comprehensive analysis of the threat to public health posed by chloroform. Based on all the information available, the Administrator will then decide whether chloroform should be regulated and if so, which regulatory mechanism under the Clean Air Act should be used. The information presented in this report includes data on emission sources of chloroform, current emission and emission control levels, emission point coordinates, and an analysis of emission reduction achievable on existing sources through use of best available control technology.

In 1982, it was estimated that 159,500 Mg of chloroform was produced. Of this amount, approximately 90 percent is used in the production of fluorocarbon 22, five percent is exported, and the remainder is used by miscellaneous sources such as laboratories, pharmaceutical companies, and dye and pesticide companies. Of the 159,500 Mg produced, known annual emissions from primary sources amount to approximately 1,840 Mg, or slightly greater than one percent of production (Table 2-1). Most emissions of chloroform to the environment result from its inadvertent formation and release (6,900 Mg/yr). Four of the source categories which contribute to its inadvertent formation and release form chloroform by the reaction of chlorine with organic precursors in water. Chloroform emissions from these four categories result from the intermedia transfer of chloroform from water to air and amount to 6,480 Mg per year. These categories include pulp and paper manufacturing, drinking water treatment plants, wastewater treatment plants, and cooling water treatment by power plants. Although these emissions are secondary, there are methods to control

TABLE 2-1. CHLOROFORM CONSUMPTION AND EMISSIONS

	Chloroform consumed, Mg/yr	Chloroform emitted, Mg/yr
PRIMARY SOURCES		
Pharmaceutical production	2,000[a]	1,000
Chloroform production	-	458
Ethylene dichloride production	-	173
Hypalon® production	b	79.7
Fluorocarbon 22 production	144,000	50.2
Oxybisphenoxarsine production	c	49.3
Grain fumigation	28.4	28.4
Subtotal	146,000	1,838.6
SECONDARY SOURCES		
Water Sources		
Pulp and paper production	-	3,890
Drinking water treatment	-	1,900
Wastewater treatment	-	424
Cooling water treatment	-	263
Air Sources		
Trichloroethylene photodegradation	-	420
Subtotal	-	6,897
Total	146,000	8,735.6

[a] Estimated

[b] Confidential

[c] Unknown

these releases, including substitution away from chloroform-forming oxidants such as free chlorine or hypochlorite to compounds such as chlorine dioxide or chloramines.

Each chapter in the document describes a chloroform source category. Chapters include pulp and paper manufacturing; ethylene dichloride production; chloroform production; fluorocarbon production; oxybisphenoxarsine/diisocyanate manufacture; pharmaceutical manufacture; trichloroethylene photodegradation; evaporation from boiler cooling water, drinking water and municipal wastewater; and grain fumigation.

One source category not discussed in this document is laboratory usage. There are approximately 109,700 laboratories in the U.S.[1] Chloroform is used in hospital, industrial, government, and university laboratories. It is used as a general reagent and in high pressure liquid chromatography (HPLC). However, aggregate data on the amount of chloroform used by laboratories could not be quantified for two reasons. First, chloroform is sold to laboratories by a variety of sources. Some is purchased directly from producers; however, most is sold by producers to distributors who buy in bulk and then repackage or reformulate the chloroform for a specific type of end use (i.e. general reagent vs. HPLC). Because the chain of distribution is so disaggregated, there is no production or distribution source to provide aggregate data on chloroform in laboratories. One distributor stated that while the company keeps records on "solvents" as a category, it does not keep detailed records for specific solvents.[2]

The second reason for lack of aggregate data stems from the fact that laboratories do not represent a homogeneous user category. Consequently, there is no central source of information from which to obtain such data for all laboratory use. However, chloroform use in laboratories does appear to be widespread. One university reported that in a survey on carcinogenic chemicals used in its 67 laboratories, chloroform was the most widely used, appearing in 53 laboratories.[3]

REFERENCES

1. Phase I Study: Profile of Laboratories with the Potential for Exposure to Toxic Substances. Prepared by Booz, Allen and Hamilton for Occupational Safety and Health Administration, Office of Regulatory Analysis, Washington, DC. March 1, 1983.

2. Telephone conversation between H. Rollins, GCA Corporation and J. Richards, J.T. Baker Chemical Company, Phillipsburg, New Jersey. November 8, 1982.

3. Survey of the use of Chemical Carcinogens in University Laboratories. University of North Carolina at Chapel Hill. Chapel Hill, North Carolina. (no date).

3. PULP AND PAPER INDUSTRY

INTRODUCTION

The pulp and paper industry is the largest chloroform emissions source category, accounting for approximately 40 percent of chloroform air emissions in the United States.[1] Chloroform is produced indirectly in process water during the bleaching of wood pulp by the reaction of chlorine and its compounds with lignins in pulp.[2] Chloroform formed in process water subsequently evaporates to the atmosphere during both the treatment of process wastewater and following treatment (from discharged mill effluent). Chloroform evaporation from process water and wastewater is the source of chloroform air emissions discussed in this chapter.

This chapter presents an overview of the pulp and paper industry, chloroform formation and fate in pulp bleaching processes, methods to reduce chloroform emissions, emission control costs for representative model plants, emissions estimates for pulp mills, and cost effectiveness of emissions control.

SOURCE DESCRIPTION

Industry Overview

The U.S. Environmental Protection Agency's Effluent Guidelines Division has identified 706 operating facilities involved in the manufacture of pulp, paper, and paperboard products.[3] The mills vary in size, age, location, raw material usage, products manufactured, production processes employed, and effluent treatment systems used. The pulp, paper, and paperboard industry consists of 3 major segments: integrated mills (where pulp alone or pulp and paper or paperboard are manufactured on-site); non-integrated mills (where paper or paperboard is manufactured but no pulp is made on-site); and secondary fibers mills (where wastepaper is used as the primary raw material). The Effluent Guidelines Division subcategorized mills with respect to raw materials, processing sequences, and types of end products made. These subcategories, which have been adopted for this report, are listed in Table 3-1.

TABLE 3-1. PULP AND PAPER MILL SUBCATEGORIES[4]

Integrated Segment

- Dissolving Kraft
- Market Bleached Kraft
- BCT Bleached Kraft
- Soda
- Unbleached Kraft
  - Linerboard
  - Bag
- Semi-Chemical
- Unbleached Kraft & Semi-Chemical
- Dissolving Sulfite Pulp
  - Nitration
  - Viscose
  - Cellophane
  - Acetate
- Papergrade Sulfite
- Groundwood - Thermo-Mechanical
- Groundwood - CMN Papers
- Groundwood - Fine Papers

Nonintegrated Segment

- Nonintegrated - Fine Papers
- Nonintegrated - Tissue Papers
- Nonintegrated - Lightweight Papers
  - Lightweight
  - Electrical
- Nonintegrated-Filter and Nonwoven Papers
- Nonintegrated-Paperboard
- Mill Groupings:
- *Integrated Miscellaneous including:
  - Alkaline-Miscellaneous
  - Groundwood Chemi-Mechanical
  - Nonwood Pulping
- *Secondary Fiber-Miscellaneous
- *Nonintegrated-Miscellaneous

Secondary Fibers Segment

- Deink
  - Fine Papers
  - Tissue Papers
  - Newsprint
- Tissue from Wastepaper
- Paperboard from Wastepaper
- Wastepaper - Molded Products
- Builders' Paper and Roofing Felt

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*Groupings of miscellaneous mills, not subcategories.

Pulping and Bleaching Process

As shown in Figure 3-1, pulp is produced by a series of steps which includes raw material preparation, pulping, and bleaching. Bleaching generally is followed by either papermaking or bundling of pulp for shipment to another papermaking mill. The major raw material for pulp manufacturing is wood. The preparation of wood for pulping includes log washing, bark removal, and chipping. Pulping is the process in which wood fibers are separated by dissolving or breaking the lignin holding the fibers together. At the end of this process, the pulp mass is brown or deeply colored due to the presence of lignins and resins.[5] Thus, it must be bleached if a white or light-colored product is to be produced.

The purification and whitening of pulp is achieved in a series of bleaching stages. Each stage consists of mixing the pulp over time with chemicals and heat, and washing the pulp after reaction to remove chemical impurities. Each stage may vary according to the chemical added, pulp consistency, temperature, time, and pH.[6] Bleach plants range from a single stage to as many as nine or ten stages. Different bleaching stages are commonly represented by symbols such as those shown in Table 3-2. The most common bleaching agents used to bleach pulp are chlorine, sodium or calcium hypochlorite, and chlorine dioxide (used in various combinations of stages). A simplified drawing of a typical bleaching sequence is shown in Figure 3-2. As the figure shows, chlorine (C) and chlorine dioxide (D) bleaching stages are separated by washing and alkaline extraction (E) stages.

In the chlorine stage, chlorine combines with lignins in the pulp forming chlorinated lignins. The chlorination reaction is extremely rapid, requiring as little as five minutes for completion. After the pulp has been saturated with chlorine, it is washed and sent to the caustic extraction stage.

Oxidized lignin is solubilized in the caustic extraction stage. In this stage, the phenolic-OH group in lignin dissolves in alkaline solution and chlorinated lignins are degraded into smaller fragments.

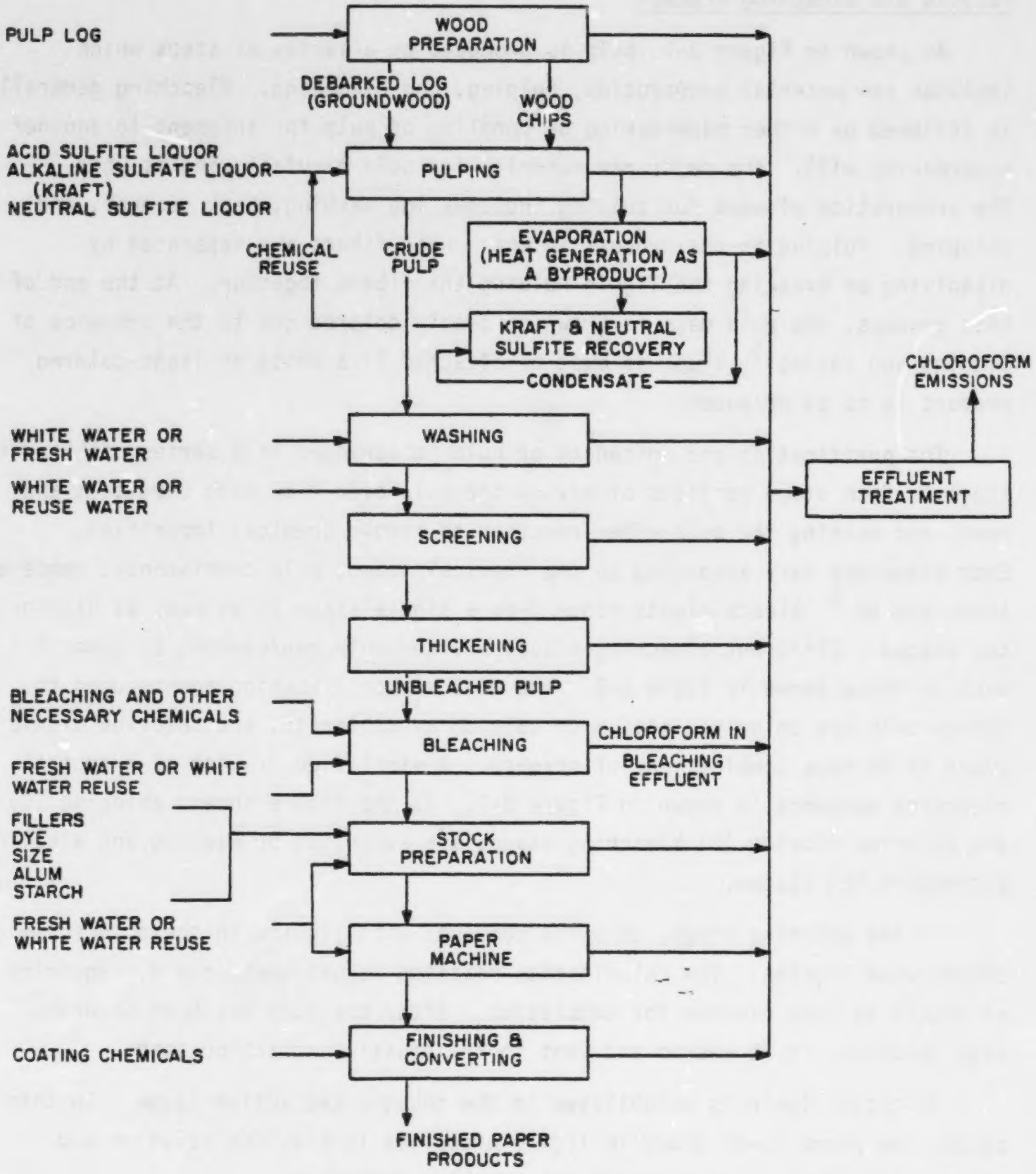
PULP LOG
WOOD PREPARATION
DEBARKED LOG (GROUNDWOOD)
WOOD CHIPS
ACID SULFITE LIQUOR
ALKALINE SULFATE LIQUOR (KRAFT)
NEUTRAL SULFITE LIQUOR
PULPING
CHEMICAL REUSE
CRUDE PULP
EVAPORATION (HEAT GENERATION AS A BYPRODUCT)
KRAFT & NEUTRAL SULFITE RECOVERY
CONDENSATE
CHLOROFORM EMISSIONS
WHITE WATER OR FRESH WATER
WASHING
WHITE WATER OR REUSE WATER
EFFLUENT TREATMENT
SCREENING
THICKENING
UNBLEACHED PULP
BLEACHING AND OTHER NECESSARY CHEMICALS
BLEACHING
CHLOROFORM IN BLEACHING EFFLUENT
FRESH WATER OR WHITE WATER REUSE
FILLERS
DYE
SIZE
ALUM
STARCH
STOCK PREPARATION
FRESH WATER OR WHITE WATER REUSE
PAPER MACHINE
COATING CHEMICALS
FINISHING & CONVERTING
FINISHED PAPER PRODUCTS

Figure 3-1. Process flow diagram for pulp and paper manufacturing process.[7]

TABLE 3-2. SYMBOLS REPRESENTING BLEACHING STAGES[8]

Name of stage	Symbol	Chemical used
Chlorination	C	Chlorine gas or chlorine water
Caustic Extraction	E	Sodium Hydroxide solution
Hypochlorite	H	Sodium or Calcium hypochlorite
Chlorine Dioxide	D	Water solution of Chlorine Dioxide
Oxygen	O	Oxygen gas and alkali
Peroxide	P	Hydrogen Peroxide (50% sol.)
Ozone	Z	Gaseous ozone (2% in Oxygen)

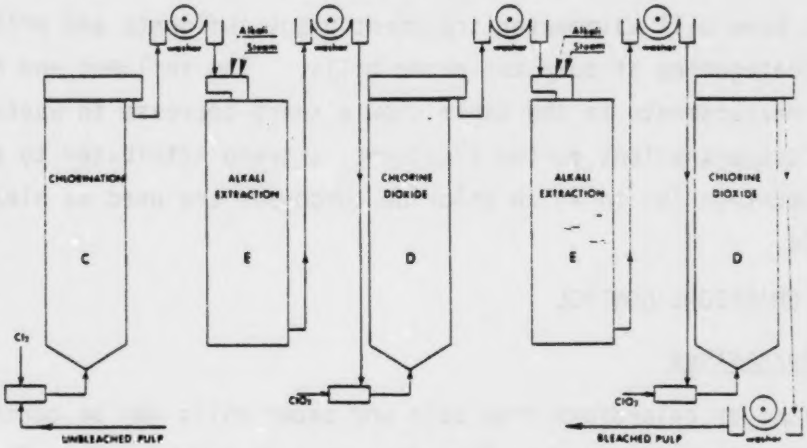
washer
Alkali
Steam
washer
washer
Alkali
Steam
washer
CHLORINATION
C
ALKALI EXTRACTION
E
CHLORINE DIOXIDE
D
ALKALI EXTRACTION
E
CHLORINE DIOXIDE
D
Cl_2
ClO_2
ClO_2
UNBLEACHED PULP
BLEACHED PULP
washer

Figure 3-2. A modern bleach sequence.[9]

Hypochlorite bleaching decolorizes and solubilizes the residual lignin, dyes, and other impurities in fiber. The bleaching reaction proceeds rapidly at first but slows down before all the lignin has reacted. Hypochlorite oxidizes cellulose (wood fiber) as well as lignin and other impurities. The oxidation of wood fibers is undesirable because it weakens the fibers and the paper products made from them. The severity of cellulose oxidation depends on temperature, pulp consistency, pH, and the amount of residual lignin compared to hypochlorite concentration.

Chlorine dioxide is often used in the final two bleaching stages in the more modern bleach plants, as shown in Figure 3-2. Bleaching with chlorine dioxide is carried out in an acidic solution, and typically degrades cellulose much less than hypochlorite.[10]

Chloroform Formation and Fate

The use of calcium or sodium hypochlorite for bleaching pulp is recognized as the major source of chloroform in the pulp and paper industry.[2] Data presented in Table 3-3 show that effluent from hypochlorite bleach stages generally contains much higher chloroform concentrations than effluent from other stages.[11]

Effluent from bleaching operations typically is discharged to on-site pulp mill wastewater treatment plants. Table 3-4 presents chloroform levels measured in some mill wastewater treatment plant influents and effluents for various subcategories of pulp and paper mills. The influent and effluent chloroform measurements in the table show a sharp decrease in wastewater chloroform concentrations during treatment, a trend attributed to evaporation.[12] The nine subcategories in which chlorine compounds are used as bleach are noted in the table.

CHLOROFORM EMISSIONS CONTROL

Control Alternatives

Emissions of chloroform from pulp and paper mills may be controlled by modifying the bleaching process to reduce or prevent chloroform formation. Because wastewater treatment plants at pulp mills treat large quantities of wastewater and often use several acres of stabilization ponds, capture of chloroform from treatment plants is not feasible by any available technology.

TABLE 3-3. AVERAGE PERCENT OF CHLOROFORM IN BLEACH PLANT EFFLUENT FORMED IN HYPOCHLORITE STAGES[a]

Bleach plant	Chloroform from hypochlorite stages, kg/Mg of pulp	Total chloroform from bleach plant kg/Mg of pulp	Percent chloroform from hypochlorite stages
A	0.54	0.62	--
B	1.78	1.84	--
C	1.65	1.68	--
D	0.18	0.26	--
E	0.25	0.43	--
F	1.12	1.16	--
TOTAL	5.52	5.99	92

[a] Reference 11.

TABLE 3-4. CHLOROFORM LEVELS IN PULP AND PAPER MILL WASTEWATER[13]

Subcategory	Total number of samples		Total number of detected analyses		Concentration range, μg/l		Average concentration, μg/l	
	Influent	Effluent	Influent	Effluent	Influent	Effluent	Influent	Effluent
Dissolving Kraft[a]	3	3	3	3	360-900	40-86	647	67
Market Bleached Kraft[a]	6	6	6	6	830-2,200	6-20	1,405	12
BCT Bleached Kraft[a]	9	9	9	8	580-4,000	0-11	1,550	6
Alkaline-Fine[a]	9	9	9	9	43-1,800	2-110	1,148	52
Unbleached Kraft Linerboard	3	3	3	0	1-2	0	1	0
Semi-Chemical	6	6	3	0	1-4	0	2	0
Unbleached Kraft and Semi-Chemical	6	6	2	0	0-6	0	3	0
Dissolving Sulfite Pulp[a]	4	4	4	4	110-360	1-42	268	13
Papergrade Sulfite[a]	12	12	12	12	62-8,600	120-1,200	2,677	433
Groundwood-Fine Papers	6	6	6	6	17-240	4-36	99	15
Deink								
Fine Papers[a]	3	3	3	3	670-9,700	95-240	4,190	145
Tissue Papers[a]	3	3	3	3	1,000-1,800	48-61	1,367	55
Newsprint	3	--	3	--	1	--	1	--
	3	3	3	3	12-46	2-10	25	5
Tissue from Wastepaper	6	6	1	0	0-9	0	3	0
	3	3	0	1	0	0-1	0	1
Paperboard from Wastepaper	15	15	11	3	0-40	0-20	15	4
	3	3	0	0	0	0	0	0
Builders' Paper & Roofing Felt	9	--	3	--	2-21	--	10	--
	3	3	0	0	0	0	0	0
Nonintegrated-Fine Papers	6	6	3	3	0-26	0-6	6	3
	3	3	3	3	4-9	4-6	7	5
Nonintegrated-Tissue Papers	6	6	3	3	2-4	4	3	4
Nonintegrated-Lightweight Papers	3	3	3	3	15-51	2-3	27	3
Integrated-Miscellaneous[a]	12	12	4	3	0-1,100	0-14	602	35
Nonintegrated-Miscellaneous	6	6	3	3	3-15	2-6	8	4
	3	3	0	0	0	0	0	0

[a] Chlorine or chlorine-containing compound is used as bleach in this subcategory.

Process modification consists of replacing hypochlorite with a chemical such as chlorine dioxide, which produces virtually no chloroform. Different bleaching chemicals have characteristic effects on pulp fibers, and for some special applications hypochlorite bleaching must be retained (the bleaching of broke, for example, which is pulp that is not baled and is reprocessed). However, chlorine dioxide can be used in a bleach sequence to obtain a brightness roughly equal to hypochlorite bleaching, and with better strength characteristics. Again, this is due to chlorine dioxide's ability to attack lignin without significantly degrading the wood fibers. The industry trend the past 15 years has been to design new pulp mills to bleach with chlorine dioxide rather than hypochlorite.[14]

Molecular oxygen, which does not react to form chloroform, has been used successfully in pulp bleaching as a separate oxidizing stage and as a chemical supplement to the alkaline extraction stage. Oxygen, used either in a separate oxidizing stage or as a supplement to the alkaline extraction stage, can be considered a partial substitute for hypochlorite in bleaching.

Four categories - dissolving sulfite pulp, dissolving kraft pulp, deink tissue, and deink fine paper - were assumed to continue using hypochlorite for technical reasons. Thus, no emission reductions are presented for these categories.

Dissolving pulps must be considered a completely separate group of fibers because the conversion of fibers into their final state involves a complex bleaching and purification process which often involves change of phase.[15] Bleach sequences for dissolving pulps were designed with hypochlorite stages playing an important part in pulp treatment. The selection of a substitute for hypochlorite in bleaching dissolving pulps poses a technical problem which is beyond the scope of this project.

The bleaching requirements of deink pulps vary widely depending on the proportions of groundwood, unbleached chemical fibers, and colored paper.[16] Often a single stage of hypochlorite is sufficient, but as many as five stages are feasible for large mills.[17] Hypochlorite is used because it is relatively inexpensive, easy to handle, and non-corrosive. Because the raw materials and the bleaching requirements in deink mills vary widely, an analysis of feasible substitutes for hypochlorite in these mills is beyond the scope of this project. Thus, mills in the deink categories were assumed to continue using hypochlorite.

Scope of Modifications

In replacing hypochlorite at a given pulp mill, several things must be considered. Bleach sequences are designed to produce a specific end product or variety of products. The sequence used depends on the type of wood used, the brightness and strength characteristics desired, the degree of flexibility desired in the sequence, and the cost. Replacing hypochlorite not only changes the sequence, but also changes the overall effect the interrelated stages have on the pulp. Thus, replacing hypochlorite entails more than merely substituting another bleaching chemical. It involves replacing an entire sequence using hypochlorite with a sequence not using hypochlorite, considering the end products and other parameters mentioned above.[18]

While a new pulp mill bleach sequence can readily be designed to use chlorine dioxide (omitting hypochlorite), differences between the two chemicals do not allow simple one-for-one replacement of hypochlorite with chlorine dioxide in existing mills. Because chlorine dioxide bleaches most effectively at a pH of 3.6, its solution is much more corrosive than typical hypochlorite bleaching solution, which has a pH of 11.[19] Thus, in an existing pulp mill, the hypochlorite equipment, such as bleach towers, washers, thick stock pumps, seal tanks, and piping, can not withstand the acidic chlorine dioxide and must be replaced.[18]

In addition to the difference in the pH of their bleaching solutions, chlorine dioxide and hypochlorite differ in their chemical action on pulp. The alkalinity of a hypochlorite bleaching solution allows the reaction products to dissolve much more readily than in the acidic chlorine dioxide solution. When hypochlorite is used, lignin reacts and goes into solution, exposing more lignin for further chemical attack. Chlorine dioxide is most effective when the pulp is washed in an alkaline solution between bleach stages to remove oxidized lignin so that more layers of lignin can be attacked. Consequently, use of chlorine dioxide may require more alkaline extraction stages in the bleach sequence than hypochlorite.[20]

Generation of chlorine dioxide must also be considered. Chlorine dioxide is highly unstable, and consequently is manufactured on-site wherever it is used in a pulp bleaching operation. To provide the amount of chlorine dioxide required in typical bleaching operations, a chlorine dioxide production process is needed, as well as raw chemical storage tanks, unloading facilities, pumps, and piping. Some pulp mills use both hypochlorite and chlorine dioxide in bleaching pulp, while other mills using hypochlorite use no chlorine dioxide and therefore have none of the equipment on-site needed to produce chlorine dioxide. For pulp mills with chlorine dioxide production equipment, the additional chlorine dioxide required to replace hypochlorite may be produced from existing excess capacity; however, excess capacity may not be available in every mill. Where chlorine dioxide is not used in bleaching, replacement of hypochlorite with chlorine dioxide would require the purchase and installation of a chlorine dioxide production plant and the appurtenances list above.[18]

In those mills where oxygen could replace or partially replace hypochlorite as a bleaching agent, equipment for adding and mixing oxygen into the pulp would be needed, as well as a tank for storing liquid oxygen on-site.

Model Mills

Because pulp mills vary in physical design and type of end product, the replacement bleach sequence should be developed on a case-by-case basis. However, several different pulp mills use a few common sequences. For this analysis, pulp mills were categorized not only based on end product, but on bleach sequence as well. The most common bleach sequences utilizing hypochlorite were identified and then grouped according to their manufacturing capacity. As a result, a large portion of U.S. mills were categorized based on bleach sequence and production capacity. Each category is represented by a "model" pulp mill characterized by a bleach sequence (utilizing hypochlorite) and production capacity. Manufacturers of pulp bleaching equipment were contacted to obtain information on feasible substitute sequences utilizing chlorine dioxide and oxygen.[18,21] The model mills, their substitute bleach sequences, and a description of the modifications involved are presented in Table 3-5.

TABLE 3-5. PROCESS MODIFICATIONS TO MODEL MILLS WITH EXISTING BLEACH PLANT SEQUENCES[18,21]

Existing sequence[a]	Production capacity and pulp process	Raw material	Sequence after modification[a]	Modifications and new equipment required
C-E-H-D	181 Mg/day Kraft	Hardwood	C-E-E_o-D	Replace H stage with E_o stage. Add new oxygen storage and mixing equipment.
		Softwood	C-E_o-D-D	Add oxygen to extraction stage; replace H stage with D stage. New D stage equipment and ClO_2 generator.
C-E-H-D	545 Mg/day Kraft	Hardwood	C-E-E_o-D	Replace H stage with E_o stage. Add new oxygen storage and mixing equipment.
		Softwood	C-E_o-D-D	Add oxygen to extraction stage; replace H stage with D stage. New D stage equipment and ClO_2 generator.
C-E-H	181 Mg/day Sulfite		C-E-D	Replace H stage with D stage. New D stage equipment, ClO_2 generator, ClO_2 chemical storage tanks, handling facilities.
C-E-H	363 Mg/day Kraft		C-E_o-D	Replace H stage with D stage. Add oxygen to extraction stage. New D stage equipment, ClO_2 generator, ClO_2 chemical storage tanks, and handling facilities.
C-E-H-E-D	545 Mg/day Kraft		C-E-D-E-D	Replace H stage with D stage. New D stage equipment and additional ClO_2 generator.
C-E-H-D-E-D	545 Mg/day Kraft		C-E-E_o-D-E-D	Add oxygen to extraction stage. Bypass H stage. Additional ClO_2 generator may be required.

[a] Key:
C = Chlorine stage
E = Caustic extraction stage
H = Sodium or calcium hypochlorite stage
D = Chlorine dioxide stage
O = Oxygen stage
E_o = Oxygen added as supplement to caustic extraction stage

Emissions and Emissions Reduction

Based on the chloroform concentration data presented in Table 3-4, chloroform emissions from each mill in the five subcategories for which controls were considered were calculated based on estimated wastewater flow and chloroform concentration. Estimated chloroform emissions for each mill are presented in Tables 3-6 through 3-10. Total annual chloroform emissions from all mills in these subcategories are estimated to be 3,340 Mg/yr.

Total chloroform production, based on influent chloroform concentrations in mills in all nine subcategories which bleach with chlorine or chlorine-containing compounds, is presented in Table 3-11. Approximately 3,890 Mg/yr of chloroform are produced from pulp bleaching and emitted from either the mill sites or the body of water receiving wastewater discharges.

Based on the data presented in Table 3-3, chloroform emissions from each pulp mill were assumed to be reduced 92 percent as the result of process modification. The estimated chloroform emission reductions at each mill are presented in Tables 3-6 through 3-10. Emission reductions range from 4.4 Mg/year to 154.5 Mg/year.

CONTROL COSTS

Control costs were estimated for eight model mills based on the modifications described in Table 3-5. The control costs for existing pulp mills were drawn from the costs for the model mill that most closely matched the bleach sequence and size of the existing mill. Where the model mills did not represent an existing mill, the costs for that mill were computed separately.

Unit chemical costs and the basis for the capital recovery factor are presented in Table 3-12. The capital costs that provide the basis for the model mill estimates are presented in Table 3-13. The chemical costs and equipment costs for bleach sequence modifications were obtained from two leading pulp bleaching equipment manufacturers and from the pulp industry.[18,21,22] The cost from the pulp industry were obtained by the National Council for Air and Stream Improvement (NCASI) from questionnaires sent to several major pulp manufacturing companies in various regions of the U.S.[22] All costs are in mid-1983 dollars. Tables 3-14 through 3-19 present the estimated total

TABLE 3-6. CHLOROFORM EMISSIONS AND EMISSION REDUCTIONS FROM MARKET BLEACHED KRAFT OPERATIONS[23]

Company	Location	Flow, 10^6 l/d	Concentration,[a] µg/l		Emission factor, µg/l	Emissions, kg/day	Emission reduction, Mg/yr
			Influent	Effluent			
Western Kraft	Hawesville, KY	25	1,633 (131)[a]	17 (2)[a]	1,616 (129)[a]	40.4 (3.2)[a]	13.6
Louisiana Pacific	Samoa, CA	95	1,405[b] (112)	12[b] (1)	1,393 (111)	132.3 (10.6)	44.4
Georgia Pacific	Zachary, LA	73	1,405 (112)	12 (1)	1,393 (111)	101.7 (8.1)	--[c]
Diamond International	Old Town, ME	65	1,405 (112)	12 (1)	1,393 (111)	90.5 (7.2)	30.4
Crown, Simpson & Fairbanks	Eureka, CA	73[d]	1,405 (112)	12 (1)	1,393 (111)	101.7 (8.1)	34.2
Brunswick Pulp	Brunswick, GA	231	1,405 (112)	12 (1)	1,393 (111)	321.8 (25.7)	108.1
Weyerhaeuser	New Bern, NC	112	1,177 (94)	7 (1)	1,170 (93)	131.0 (10.5)	44.0
Weyerhaeuser	Everett, WA	95	1,405 (112)	12 (1)	1,393 (111)	132.3 (10.6)	44.4
Consolidated Papers	Wisconsin Rapids, WI	29	1,405 (112)	12 (1)	1,393 (111)	40.4 (3.2)	--[c]
Scott Paper	Hinckley, ME	73[d]	1,405 (112)	12 (1)	1,393 (111)	101.7 (8.1)	--[c]
Hammermill	Selma, AL	77	1,405 (112)	12 (1)	1,393 (111)	107.3 (8.6)	--[c]
Proctor & Gamble	Oglethorpe, GA	73[d]	1,405 (112)	12 (1)	1,393 (111)	101.7 (8.1)	--[c]

[a] Number in parentheses are chloroform levels after 92 percent reduction.

[b] Average influent and effluent concentrations for market bleached kraft operations are based on tests conducted at Western Kraft, Hawesville, KY; and Weyerhaeuser, New Bern, NC.

[c] Hypochlorite is not used in the bleach sequence at this mill.

[d] Average flow for all market bleached kraft operations, corrected for product throughput.

TABLE 3-7. CHLOROFORM EMISSIONS AND EMISSION REDUCTIONS FROM BCT BLEACHED KRAFT OPERATIONS[23]

Company	Location	Flow, 10^6 l/d	Concentration,[a] µg/l Influent	Concentration,[a] µg/l Effluent	Emission factor, µg/l	Emissions, kg/day	Emission reduction, Mg/yr
James River	Butler, AL	163	877 (70)[a]	6 (1)[a]	871 (69)[a]	142.0 (11.4)[a]	47.7
James River	Halsey, OR	50	1,550[b] (124)	6[b] (1)	1,544 (123)	77.2 (6.2)	25.9
Temple Eastex	Diboll, TX	184	1,550 (124)	6 (1)	1,544 (123)	284.1 (22.7)	95.4
Continental Forest	Augusta, GA	117	1,550 (124)	6 (1)	1,544 (123)	180.6 (14.4)	60.7
Potlatch Corp.	Lewiston, ID	126	1,550 (124)	6 (1)	1,544 (123)	194.5 (15.6)	65.3
Federal Paperboard	Riegelwood, NC	132	2,833 (227)	2 (1)	2,831 (226)	373.7 (29.9)	125.5
International Paper	Texarkana, TX	84	1,550 (124)	6 (1)	1,544 (123)	129.7 (10.4)	43.5
Gulf States Paper	Demopolis, AL	69	940 (75)	10 (1)	930 (74)	64.2 (5.1)	--[c]
Potlatch Corp.	McGhee, AR	116	1,550 (124)	6 (1)	1,544 (123)	179.1 (14.3)	--[c]

[a] Numbers in parentheses are the chloroform levels after 92 percent reduction.

[b] Average influent and effluent concentrations for BCT bleached kraft operations are based on tests conducted at James River, Butler, AL; Federal Paperboard, Riegelwood, NC; and Gulf States Paper, Demopolis, AL.

[c] Hypochlorite is not used in the bleach sequence at this mill.

TABLE 3-8. CHLOROFORM EMISSIONS AND EMISSION REDUCTIONS FROM SODA AND KRAFT FINE PAPER OPERATIONS[23]

Company	Location	Flow, 10^6 l/d	Concentration,[a] μg/l Influent	Concentration,[a] μg/l Effluent	Emission factor, μg/l	Emissions, kg/day	Emission reduction, Mg/yr
Appleton Papers	Roaring Spring, PA	16	1,148 (92)	52(4)	1,096 (88)	17.5 (1.4)	--[b]
Scott Paper	Westbrook, ME	61	1,148 (92)	52(4)	1,096 (88)	66.9 (1.4)	22.5
Scott Paper	Muskegon, MI	37	1,148 (92)	52(4)	1,096 (88)	40.6 (1.4)	13.7
Simpson Paper	Anderson, CA	44	1,148 (92)	52(4)	1,096 (88)	48.2 (1.4)	--[b]
P.H. Glatfelter	Spring Grove, PA	49	1,400(112)	110(9)	1,290(103)	63.2 (5.0)	21.2
International Paper	Jay, ME	116	1,148 (92)	52(4)	1,096 (88)	127.1(10.2)	--[b]
International Paper	Ticonderoga, NY	63	1,081 (86)	52(4)	1,029 (82)	69.0 (5.5)	--[b]
International Paper	Bastrop, LA	59	1,148 (92)	52(4)	1,096 (88)	64.7 (5.2)	21.7
Champion International	Pasadena, TX	130	1,148 (92)	52(4)	1,096 (88)	142.5(11.4)	47.9
Champion International	Courtland, AL	84	963 (77)	4(1)	959 (76)	80.6 (6.4)	27.1
Boise Cascade	Rumford, ME	95	1,148 (92)	52(4)	1,096 (88)	104.1 (8.3)	35.0
Westvaco	Luke, MD	77	1,148 (92)	52(4)	1,096 (88)	84.4 (6.8)	28.3
Nekoosa	Port Edwards, WI	43	1,148 (92)	52(4)	1,096 (88)	47.1 (3.8)	15.8
Nekoosa	Ashdown, AR	79	1,148 (92)	52(4)	1,096 (88)	86.6 (6.9)	--[b]
Pentech Papers	Johnsonburg, PA	37	1,148 (92)	52(4)	1,096 (88)	40.6 (3.2)	13.6
Mead Papers	Escanaba, MI	64	1,148 (92)	52(4)	1,096 (88)	70.1 (5.6)	--[b]
Mead Papers	Chillicothe, OH	116	1,148 (92)	52(4)	1,096 (88)	127.1(10.2)	42.7
Boise Cascade	International Falls, MN	89	1,148 (92)	52(4)	1,096 (88)	97.5 (7.8)	32.7
Hammermill	Erie, PA	47	1,148 (92)	52(4)	1,096 (88)	51.5 (4.1)	17.3
Mead Papers	Kingsport, TN	45	1,148 (92)	52(4)	1,096 (88)	49.3 (3.9)	16.6

[a] Average influent and effluent concentrations for soda and kraft fine paper operations are based on tests conducted at P.H. Glatfelter, Spring Grove, PA; International Paper, Ticonderoga, NY; and Champion International, Courtland, AL. Numbers in parentheses are chloroform levels after 92 percent reduction.

[b] Hypochlorite is not used in the bleach sequence at this mill.

TABLE 3-9. CHLOROFORM EMISSIONS AND EMISSION REDUCTIONS FROM PAPERGRADE SULFITE OPERATIONS[23]

Company	Location	Flow, 10^6 l/d	Concentration,[a] µg/l		Emission factor, µg/l	Emissions, kg/day	Emission reduction, Mg/yr
			Influent	Effluent			
Georgia Pacific	Bellingham, WA	155	2,677(214)	433(34)	2,244(180)	347.8(27.8)	116.8
Scott Paper	Everett, WA	205	2,677(214)	433(34)	2,244(180)	460.0(36.8)	154.5
Nekoosa	Port Edwards, WI	43	2,677(214)	433(34)	2,244(180)	96.5 (7.7)	32.4
St. Regis Paper	Rhinelander, WI	58	2,677(214)	433(34)	2,244(180)	130.2(10.4)	43.7
Flambeau Paper	Park Falls, WI	25	2,677(214)	433(34)	2,244(180)	56.1 (4.5)	18.8
Boise Cascade	Salem, OR	60	2,677(214)	433(34)	2,244(180)	134.6(10.8)	45.2
Wausau Paper	Brokaw, WI	36	2,677(214)	433(34)	2,244(180)	80.8 (6.5)	27.1
Badger Paper	Peshtigo, WI	6	2,677(214)	433(34)	2,244(180)	13.5 (1.1)	4.5
Consolidated Papers	Appleton, WI	6	2,677(214)	433(34)	2,244(180)	13.5 (1.1)	4.5
Finch Pruyn & Co.	Glen Falls, NY	69	2,677(214)	433(34)	2,244(180)	154.8(12.4)	52.0
Weyerhaeuser	Rothschild, WI	44	2,677(214)	433(34)	2,244(180)	98.7 (7.9)	33.1
James River	Green Bay, WI	6	2,677(214)	433(34)	2,244(180)	13.5 (1.1)	4.5
Proctor & Gamble	Mehoopany, PA	36	2,677(214)	433(34)	2,244(180)	80.8 (6.5)	27.1
Proctor & Gamble	Green Bay, WI	64	2,677(214)	433(34)	2,244(180)	143.6(11.5)	48.2

[a] Papergrade sulfite influent and effluent concentrations are based on tests conducted at Wausau Paper, Brokaw, Wi. Numbers in parentheses are chloroform levels after 92 percent reduction.

TABLE 3-10. CHLOROFORM EMISSIONS AND EMISSION REDUCTIONS FROM MISCELLANEOUS INTEGRATED OPERATIONS[23]

Company	Location	Flow, 10^6 l/d	Concentration,[a] µg/l		Emission factor, µg/l	Emissions, kg/day	Emission reduction, Mg/yr
			Influent	Effluent			
Longview Fiber	Longview, WA	210	602 (48)	35 (3)	567 (45)	119.1 (9.5)	40.0
Boise Southern	Deridder, LA	74	602 (48)	35 (3)	567 (45)	42.0 (3.4)	14.1
St. Regis Paper	Tacoma, WA	100	602 (48)	35 (3)	567 (45)	56.7 (4.5)	19.0
St. Regis Paper	Cantonment, FL	88	602 (48)	35 (3)	567 (45)	50.0 (4.0)	16.8
St. Joe Paper	Port St. Joe, FL	104	602 (48)	35 (3)	567 (45)	59.0 (4.7)	19.8
Chesapeake Corp.	West Point, VA	45	602 (48)	35 (3)	567 (45)	25.5 (2.0)	--[b]
Hoerner Waldorf	Missoula, MT	54	602 (48)	35 (3)	567 (45)	30.6 (2.4)	10.3
Hudson Pulp & Paper	Palatka, FL	140	602 (48)	35 (3)	567 (45)	79.4 (6.4)	26.7
Crown Zellerbach	Bogalusa, LA	101[c]	602 (48)	35 (3)	567 (45)	57.3 (4.6)	19.2
SW Forest Industries	Snowflake, AZ	101[c]	602 (48)	35 (3)	567 (45)	57.3 (4.6)	19.2
International Paper	Panama City, FL	93	602 (48)	35 (3)	567 (45)	52.7 (4.2)	17.7
International Paper	Georgetown, SC	106	602 (48)	35 (3)	567 (45)	60.1 (4.8)	20.2
Fiberboard Corp.	Antioch, CA	101[c]	602 (48)	35 (3)	567 (45)	57.3 (4.6)	19.2
Brown Co.	Berlin, NH	72	70 (6)	30 (2)	40 (3)	2.9 (0.2)	--[b]
Weyerhaeuser	Plymouth, NC	101	602 (48)	35 (3)	567 (45)	52.7 (4.2)	17.7
Gilman Paper	St. Mary's, GA	146	602 (48)	35 (3)	567 (45)	82.8 (6.6)	--[b]
Georgia Pacific	Crossett, AR	173	602 (48)	35 (3)	567 (45)	98.1 (7.8)	32.9
Westvaco	Wickliffe, KY	87	602 (48)	35 (3)	567 (45)	49.3 (3.9)	--[b]
Scott Paper	Mobile, AL	101[c]	602 (48)	35 (3)	567 (45)	57.3 (4.6)	19.2
Container Corp. of America	Brewton, AL	135	602 (48)	35 (3)	567 (45)	76.5 (6.1)	--[b]
Crown Zellerbach	Camas, WA	276	904 (72)	66 (5)	838 (67)	231.3 (18.5)	77.7
Georgia Pacific	Woodland, ME	121	602 (48)	35 (3)	567 (45)	68.6 (5.5)	23.0
Bowater Carolina	Catawba, SC	132	602 (48)	35 (3)	567 (45)	74.8 (6.0)	25.1
Potlatch Corp.	Cloquet, MN	54	602 (48)	35 (3)	567 (45)	30.6 (2.4)	10.3
Weyerhaeuser	Longview, WA	151	602 (48)	35 (3)	567 (45)	85.6 (6.8)	28.7
International Paper	Pine Bluff, AR	114	602 (48)	35 (3)	567 (45)	64.6 (5.2)	21.7
International Paper	Moss Point, MS	94	602 (48)	35 (3)	567 (45)	53.3 (4.3)	17.9

CONTINUED

TABLE 3-10. (continued)

Company	Location	Flow, 10^6 l/d	Concentration,[a] µg/l		Emission factor, µg/l	Emissions, kg/day	Emission reduction, Mg/yr
			Influent	Effluent			
Boise Cascade	St. Helens, OR	125	602 (48)	35 (3)	567 (45)	70.9 (5.7)	23.8
Lincoln Pulp & Paper	Lincoln, ME	101[c]	602 (48)	35 (3)	567 (45)	57.3 (4.6)	--[b]
Allied Paper	Jackson, AL	101[c]	602 (48)	35 (3)	567 (45)	57.3 (4.6)	19.3
Champion International	Canton, NC	182	602 (48)	35 (3)	567 (45)	103.2 (8.3)	34.7
Westvaco	Covington, VA	99	602 (48)	35 (3)	567 (45)	56.1 (4.5)	18.8
International Paper	Mobile, AL	117	602 (48)	35 (3)	567 (45)	66.3 (5.3)	--[b]
Crown Zellerbach	St. Francisville, LA	101[c]	602 (48)	35 (3)	567 (45)	57.3 (4.6)	19.3
Crown Zellerbach	Clatskanie, OR	101[c]	602 (48)	35 (3)	567 (45)	57.3 (4.6)	19.3
Union Camp	Franklin, VA	114	602 (48)	35 (3)	567 (45)	64.6 (5.2)	--[b]
Kimberly Clark	Coosa Pines, AL	101[c]	602 (48)	35 (3)	567 (45)	57.3 (4.6)	--[b]
Southland Paper Mills	Lufkin, TX	71	602 (48)	35 (3)	567 (45)	40.3 (3.2)	13.5
Bowater Southern	Calhoun, TN	140	602 (48)	35 (3)	567 (45)	79.4 (6.4)	76.7
Alpha Cellulose	Lumberton, NC	3	833 (67)	10 (1)	733 (58)	2.2 (0.2)	--[b]
Valentine Pulp & Paper	Lockport, LA	23	602 (48)	35 (3)	567 (45)	13.0 (1.0)	4.4
Hercules, Inc.	Hopewell, VA	38	602 (48)	35 (3)	567 (45)	21.5 (1.7)	7.2
Olin Corp.	Pisgah Forest, NC	98	602 (48)	35 (3)	567 (45)	55.6 (4.4)	18.7
Southland Paper	Houston, TX	53	602 (48)	35 (3)	567 (45)	30.1 (2.4)	10.1

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[a] Average influent and effluent concentrations for miscellaneous integrated operations are based on tests conducted at Brown Co., Berlin, NH; Crown Zellerbach, Camas, WA; and Alpha Cellulose, Lumberton, NC. Numbers in parentheses are chloroform levels after 92 percent reduction.

[b] Hypochlorite is not used in bleach sequence at this mill.

[c] Average flow for miscellaneous integrated operations, corrected for product throughput.

TABLE 3-11. SUMMARY OF TOTAL CHLOROFORM PRODUCTION IN PULP AND PAPER MILLS

Mill subcategory	Total chloroform production (kg/day)	Total chloroform production (Mg/yr)
Market Bleached Kraft	1,414.6[a]	516.3
BCT Bleached	1,631.2[a]	595.4
Soda and Kraft Fine Paper	1,547.9[a]	565.0
Papergrade Sulfite	2,176.4[a]	794.4
Miscellaneous Integrated	2,835.4[a]	1,034.9
Dissolving Kraft	382.6[b]	139.6
Dissolving Sulfite	216.5[b]	79.0
Deink Fine	338.0[b]	123.4
Deink Tissue	104.1[b]	38.0
TOTAL	10,646.7	3,886.0

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[a] Based on the influent chloroform concentrations presented in Tables 3-6 through 3-10.

[b] Calculated by multiplying individual mill wastewater flows by average or measured wastewater influent chloroform concentrations. Data were obtained from verification sampling data in Docket WH-552, available to the public at the Public Information Reference Unit, U.S. Environmental Protection Agency, Washington, DC.

TABLE 3-12. BASIS FOR CAPITAL COST ESTIMATES.

1. Capital recovery factor for capital charges (10 percent interest and 16-year life)	0.128 x capital
2. Annual maintenance charges	0.05 x capital
3. Annual miscellaneous charges (taxes, insurance, administration)	0.04 x capital
TOTAL ANNUALIZED COST FACTOR	0.218 x capital
4. Chemical costs (dollars/Mg)[a]	
• Hypochlorite	385[b]
• Chlorine dioxide	1,325[c]
• Oxygen	225[d]
• Sodium hydroxide	250

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[a] Costs are based on comments from industry supplied by NCASI (mid-1983 dollars).

[b] While actual costs can be significantly lower or higher, this figure represents a reasonable average of costs quoted in the comments received.

[c] This cost assumes no recovery credit for by-product hypochlorite produced in scrubber controlling chlorine emission from ClO_2 generating process.

[d] Includes cost of magnesium salts added for resistance to fiber attack.

TABLE 3-13. CAPITAL AND ANNUAL COSTS FOR BLEACH PLANT MODIFICATIONS[18,21,22] (mid-1983 dollars)

Cost items for pulp mills	Capital cost ($1000)	Annual cost ($1000)[a]
1. Install chlorine dioxide bleaching stage in place of hypochlorite bleaching stage		
• 181 Mg/day mill	3,000	654
• 363 Mg/day mill	3,500	763
• 545 Mg/day mill	4,000	872
2. Install additional chlorine dioxide generating plant on site (5.45 Mg/day ClO_2 production capacity)	4,200	916
3. Storage tanks, handling facilities, pumps, and piping for chlorine dioxide and chlorine dioxide feedstock chemcials at mills where chlorine dioxide is not presently used		
• 181 Mg/day mill	750	164
• 363 Mg/day mill	1,000	218
4. Install oxygen addition equipment to caustic extraction stage (All mill capacities)	500	109

[a] Capital costs annualized with a factor of 0.218, the sum of the factors for capital recovery, maintenance, and miscellaneous charges presented in Table 3-12.

TABLE 3-14. ESTIMATED TOTAL ANNUAL COST OF MODIFYING C-E-H-D BLEACH SEQUENCE FOR HARDWOOD TO C-E-E_O-D SEQUENCE (mid-1983 dollars)

Mill size (Mg/day) and cost items	Annual costs ($1000)
181 Mg/day	
1. Hypochlorite stage converted to caustic extraction stage with oxygen addition	$ 109
2. Additional chemicals:	
• Sodium hydroxide, 8 kg/Mg	132
• Chlorine dioxide 2 kg/Mg	175
• Oxygen, 4 kg/Mg	59
3. Rental of oxygen storage tank	12
4. Hypochlorite cost, as savings, 12.5 kg/Mg	- 318
TOTAL NET COST	$ 168
545 Mg/day	
1. Hypochlorite stage converted to caustic extraction stage with oxygen addition	$ 109
2. Additional chemicals:	
• Sodium hydroxide, 8 kg/Mg	398
• Chlorine dioxide, 2 kg/Mg	526
• Oxygen, 4 kg/Mg	177
3. Rental of oxygen storage tank	12
4. Hypochlorite cost, as savings, 12.5 kg/Mg	- 957
TOTAL NET COST	$ 265

TABLE 3-15. ESTIMATED TOTAL ANNUAL COST OF MODIFYING C-E-H-D BLEACH SEQUENCE FOR SOFTWOOD TO C-E_o-D-D (mid-1983 dollars)

Mill size (Mg/day) and cost items	Annual costs ($1000)
181 Mg/day	
1. Chlorine dioxide bleach stage, installed	$ 654
2. Chlorine dioxide generator, installed	916
3. Chlorine dioxide chemical, 5 kg/Mg	437
4. Oxygen handling and mixing equipment, installed	109
5. Oxygen added to caustic extraction stage, 5 kg/Mg	74
6. Oxygen storage tank rental	12
7. Hypochlorite cost, as savings, 20 kg/Mg	- 509
TOTAL NET COST	$ 1,693
545 Mg/day	
1. Chlorine dioxide bleach stage, installed	$ 763
2. Chlorine dioxide generator, installed	916
3. Chlorine dioxide chemical, 5 kg/Mg	1,315
4. Oxygen handling and mixing equipment, installed	109
5. Oxygen added to caustic extraction stage, 5 kg/Mg	222
6. Oxygen storage tank rental	12
7. Hypochlorite cost, as savings, 20 kg/Mg	-1,532
TOTAL NET COST	$ 1,805

TABLE 3-16. ESTIMATED TOTAL ANNUAL COST OF MODIFYING C-E-H SULFITE PULP BLEACH SEQUENCE TO C-E-D FOR 181 Mg/DAY MILL (mid-1983 dollars)

Cost items	Annual costs ($1000)
1. Chlorine dioxide bleach stage, installed	$ 654
2. Chlorine dioxide generator, installed	916
3. Chlorine dioxide chemical, 5 kg/Mg	524
4. Storage tanks, handling facilities, pumps, and piping for chlorine dioxide feedstock chemicals	164
5. Hypochlorite cost, as savings, 15 kg/Mg	- 382
TOTAL NET COST	$ 1,876

TABLE 3-17. ESTIMATED TOTAL ANNUAL COST OF MODIFYING C-E-H KRAFT PULP BLEACH SEQUENCE TO C-E_o-D FOR 363 Mg/DAY MILL (mid-1983 dollars)

Cost items	Annual costs ($1000)
1. Oxygen handling and mixing equipment	$ 109
2. Oxygen added to caustic extraction stage, 5 kg/Mg	148
3. Oxygen storage tank rental	12
4. Chlorine dioxide bleach stage, installed	763
5. Chlorine dioxide generator, installed	916
6. Chlorine dioxide chemical, 6 kg/Mg	1,051
7. Storage tanks, handling facilities, pumps, and piping for chlorine dioxide feedstock chemicals	218
8. Hypochlorite cost, as savings, 20 kg/Mg	-1,020
TOTAL NET COST	$ 2,197

TABLE 3-18. ESTIMATED TOTAL ANNUAL COST FOR MODIFYING C-E-H-E-D KRAFT MILL BLEACH SEQUENCE TO C-E_o-D-E-D FOR 545 Mg/DAY MILL (mid-1983 dollars)

Cost items	Annual costs ($1000)
1. Chloride dioxide bleach stage, installed	$ 872
2. Chlorine dioxide generator, installed	916
3. Chlorine dioxide chemical, 7 kg/Mg	1,841
4. Oxygen handling and mixing equipment, installed	109
5. Oxygen added to caustic extraction stage, 5 kg/Mg	39
6. Oxygen storage tank rental	12
7. Hypochlorite cost, as savings, 25 kg/Mg	-1,915
TOTAL NET COST	$ 1,850

TABLE 3-19. ESTIMATED TOTAL ANNUAL COST OF MODIFYING C-E-H-D-E-D KRAFT PULP BLEACH SEQUENCE TO C-E-E_o-D-E-D FOR 545 Mg/DAY MILL (mid-1983 dollars)

Cost items	Annual costs ($1000)
1. Oxygen handling and mixing equipment, installed	$ 109
2. Oxygen added to caustic extraction stage, 5 kg/Mg	222
3. Sodium hydroxide added, 8 kg/Mg	398
4. Oxygen storage tank rental	12
5. Hypochlorite cost, as savings, 10 kg/Mg	- 766
TOTAL NET COST	$ - 25 (net savings)

annualized control costs for the eight model mills. The model mill control costs range from a net savings of $25,000 per year (due to reduced chemical costs) to a net cost of $2.2 million per year.

Estimated annual control costs for each existing pulp mill presently using hypochlorite are given in Tables 3-20 through 3-24. Annualized control costs range from a net savings of $25,000 per year to a net cost of $5.55 million per year.

COST-EFFECTIVENESS

The cost-effectiveness of control for each existing pulp mill was computed from estimated annual control costs and the estimated emission reductions shown in Tables 3-6 through 3-10 and is listed for each mill in Tables 3-20 through 3-24. Table 3-25 presents a summary of control cost-effectiveness for each subcategory. Cost-effectiveness ranges from a net savings of $1,400 per Mg to a net cost of $417,000 per Mg.

TABLE 3-20. ESTIMATED ANNUALIZED COSTS AND COST EFFECTIVENESS OF BLEACH SEQUENCE MODIFICATIONS IN MARKET BLEACHED KRAFT MILLS[20]

Company	Location	Pulp production rate, Mg/day	Existing bleach sequence	Modification for chloroform control	Annualized cost, \$1000[a]	Cost-effectiveness, \$1000/Mg $CHCl_3$
Western Kraft	Hawesville, KY	335	CEHED	CEDED	1,850	136
Louisiana Pacific	Samoa, CA	528	CEHDED	CEE_oDED	(25)	(0.563)
Georgia Pacific	Zachary, LA	538	CEDED	none	NA[b]	--
Diamond International	Old Town, ME	545	CEHDD	CEE_oDD	(25)	(0.822)
Crown, Simpson & Fairbanks	Eureka, CA	458	CEHDEDPS	CEE_oDEDPS	(25)	(0.731)
Brunswick Pulp	Brunswick, GA	590	CHDED	CE_oDED	(25)	(0.231)
		318			(25)	(0.231)
		318			(25)	(0.231)
Weyerhaeuser	New Bern, NC	647	CEHED	CEDED	1,850	42
Weyerhaeuser	Everett, WA	302	CEHED	CEDED	1,850	41.7
Consolidated Papers	Wisconsin Rapids, WI	371	CEDED	none	NA	--
Scott Paper	Hinckley, ME	458	CEDED	none	NA	--
Hammermill	Selma, AL	481	CEDED	none	NA	--
Proctor & Gamble	Oglethorpe, GA	458	Confidential[c]	--	--	--

[a] Numbers in parentheses represent a net savings.

[b] Not applicable.

[c] Monitoring has shown no chloroform in the mill effluent.

TABLE 3-21. ESTIMATED ANNUALIZED COSTS AND COST EFFECTIVENESS OF BLEACH SEQUENCE MODIFICATIONS IN BCT BLEACHED KRAFT MILLS[20]

Company	Location	Pulp production rate, Mg/day	Existing bleach sequence	Modification for chloroform control	Annualized cost, \$1000[a]	Cost-effectiveness, \$1000/Mg $CHCl_3$
James River	Butler, AL	500	CEHD	CE$_o$DD	1,805	37.8
		500	CEHD	CE$_o$DD	1,805	69.7
James River	Halsey, OR	272	CEHH	CE$_o$D	2,197	23.0
Temple Eastex	Diboll, TX	500	CEHED	CEDED	1,850	30.5
Continental Forest	Augusta, GA	703	CEHD	CE$_o$DD	1,805	27.6
Potlatch Corp.	Lewiston, ID	800	CEHED	CEDED	1,850	14.7
		250	CEHD	CE$_o$DD	1,693	13.5
Federal Paperboard	Riegelwood, NC	350	CEHDED	CEE$_o$DED	(25)	(0.575)
International Paper	Texarkana, TX	480	CEHD	CE$_o$DD	1,805	41.5
Gulf States Paper	Demopolis, AL	463	CEDED	none	NA[b]	--
Potlatch Corp.	McGhee, AR	410	CEDED	none	NA	--

[a] Numbers in parentheses represent a net savings.

[b] Not applicable.

TABLE 3-22. ESTIMATED ANNUALIZED COSTS AND COST EFFECTIVENESS OF BLEACH SEQUENCE MODIFICATIONS IN SODA AND KRAFT FINE BLEACHED PAPER MILLS[20]

Company	Location	Pulp production rate, Mg/day	Existing bleach sequence	Modification for chloroform control	Annualized cost, $1000[a]	Cost-effectiveness, $1000/Mg $CHCl_3$
Appleton Papers	Roaring Spring, PA	167	D/CED	none	NA[b]	--
Scott Paper	Westbrook, ME	227	CEHD	CE$_o$DD	1,693	75.2
Scott Paper	Muskegon, MI	227	CEHD	CE$_o$DD	1,693	123.6
Simpson Paper	Anderson, CA	163	CEDED	none	NA	--
P.H. Glatfelter	Spring Grove, PA	446	CHHD	CEE$_o$D	1,805	85.1
International Paper	Jay, ME	418	CEDED	none	NA	--
International Paper	Ticonderoga, NY	536	CEDED	none	NA	--
International Paper	Bastrop, LA	508	CEHD	CEE$_o$D	265	12.2
			CEHDD	CEE$_o$DD	1,805	37.7
Champion International	Pasadena, TX	663	CHEDH	CE$_o$DD	1,805	66.6
Champion International	Courtland, AL	580	CEHDH	CE$_o$DD	1,805	51.6
Boise Cascade	Rumford, ME	544	CEHD	CE$_o$DD	1,805	63.8
Westvaco	Luke, MD	656	CEHD	CE$_o$DD	1,805	114.2
Nekoosa	Ashdown, AR	498	CEDED	none	NA	--
Pentech Papers	Johnsonburg, PA	164	CEHP	CE$_o$DP	2,197	161.5
Mead Papers	Escanaba, MI	545	CEDED	none	NA	--
Mead Papers	Chillicothe, OH	545	CEHD	CEE$_o$D	265	6.2
Boise Cascade	International Falls, MN	309	CHEHH	CE$_o$DD	2,960	90.5
Hammermill	Erie, PA	486	CEHD	CEE$_o$D	265	15.3
Mead Papers	Kingsport, TN	227	CEHP	CE$_o$DP	2,197	132.3

[a] Numbers in parentheses represent a net savings.

[b] Not applicable.

[c] Cost from Table 3-16.

[d] Cost from Table 3-16, plus cost of additional chlorine dioxide stage.

TABLE 3-23. ESTIMATED ANNUALIZED COSTS AND COST EFFECTIVENESS OF BLEACH SEQUENCE MODIFICATIONS FOR CONTROL OF CHLOROFORM IN PAPERGRADE SULFITE MILLS[20]

Company	Location	Pulp production rate, Mg/day	Existing bleach sequence	Modification for chloroform control	Annualized cost, \$1000[a]	Cost-effectiveness, \$1000/Mg $CHCl_3$
Georgia Pacific	Bellingham, WA	448	CEHDP	CEE_oDP	1,805	15.5
Scott Paper	Everett, WA	875	CHH	CE_oD	2,197	14.2
Nekoosa	Port Edwards, WI	210	CEH	CE_oD	2,197	67.8
St. Regis Paper	Rhinelander, WI	55	CEH	CED	1,876	42.9
Flambeau Paper	Park Falls, WI	100	HP	CED	1,876	99.8
Boise Cascade	Salem, OR	229	CEH	CE_oD	2,197	48.6
Wausau Paper	Brokaw, WI	170	CEH	CED	1,876	69.2
Badger Paper	Peshtigo, WI	78	CEH	CED	1,876	416.9
Consolidated Papers	Appleton, WI	141	CEH	CED	1,876	416.9
Finch Pruyn & Co.	Glen Falls, NY	245	CEH	CED	1,876	36.0
Weyerhaeuser	Rothschild, WI	181	CEH	CED	1,876	56.7
James River	Green Bay, WI	112	H	CED	1,876	416.9
Proctor & Gamble	Mehoopany, PA	373	CEH	CE_oD	2,197	81.0
Proctor & Gamble	Green Bay, WI	373	CEH	CE_oD	2,197	45.6

[a] Numbers in parentheses represent a net savings.

TABLE 3-24. ESTIMATED ANNUALIZED COSTS AND COST EFFECTIVENESS OF BLEACH SEQUENCE MODIFICATIONS IN MISCELLANEOUS INTEGRATED MILLS[20]

Company	Location	Pulp production rate, Mg/day	Existing bleach sequence	Modification for chloroform control	Annualized cost, \$1000[a]	Cost-effectiveness, \$1000/Mg $CHCl_3$
Longview Fiber	Longview, WA	223	CEHD	CE$_o$DD	1,693	42.3
Boise Southern	Deridder, LA	149	CEH	CED	1,876	133.0
St. Regis Paper	Tacoma, WA	161	CCEHH	CCE$_o$D	1,693	89.1
St. Regis Paper	Cantonment, FL	250	CEHDEH	CEE$_o$DED	1,942	115.6
St. Joe Paper	Port St. Joe, FL	202	CEHD	CE$_o$DD	1,693	85.5
Chesapeake Corp.	West Point, VA	211	D/C-O-D	none	NA	--
Hoerner Waldorf	Missoula, MT	127	CHHD	CE$_o$DD	1,693	164.4
Hudson Pulp & Paper	Palatka, FL	112	CEHD	CE$_o$DD	1,693	63.4
Crown Zellerbach	Bogalusa, LA	181	CEHD	CE$_o$DD	1,693	88.0
SW Forest Industries	Snowflake, AZ	90	CEH	CED	1,876	97.7
International Paper	Panama City, FL	555	CEHDED	CEE$_o$DED	(25)	(1.4)
International Paper	Georgetown, SC	318	CEHDH	CEE$_o$DD	1,805	89.3
Fiberboard Corp.	Antioch, CA	181	CEHPH	CE$_o$DP	1,693	88.0
Brown Co.	Berlin, NH	636	CEDED	none	NA	--
Weyerhaeuser	Plymouth, NC	472	CEHEDP	CEDEDP	1,850	104.5
Gilman Paper	St. Mary's, GA	434	CEDED	none	NA	--
Georgia Pacific	Crossett, AR	636	CEHDED	CEE$_o$DED	(25)	(0.8)
Westvaco	Wickliffe, KY	533	CEDED	none	NA	--
Scott Paper	Mobile, AL	400 400 400	CEHED	CEDED	5,550	289.1
Container Corp. of America	Brewton, AL	563	CEDED	none	NA	--
Crown Zellerbach	Camas, WA	1,044	CEHED	CEDED	2,166	27.9
Georgia Pacific	Woodland, ME	560	CEHDED	CEE$_o$DED	(25)	(1.1)
Bowater Carolina	Catawba, SC	908	CEHED	CEDED	2,166	86.3
Potlatch Corp.	Cloquet, MN	353	CEHED	CEDED	1,850	179.6
Weyerhaeuser	Longview, WA	181	CEHD	CE$_o$DD	1,693	59.0
		363	CEHD	CE$_o$DD	1,693	59.0
		270	CN$_H$HEHP	CNE$_o$DP	1,693	59.0
International Paper	Pine Bluff, AR	990	CEHD	CE$_o$DD	2,246	103.5
International Paper	Moss Point, MS	591	CEHDED	CEE$_o$DED	(25)	(1.4)

CONTINUED

TABLE 3-24. (continued)

Company	Location	Pulp production rate, Mg/day	Existing bleach sequence	Modification for chloroform control	Annualized cost, \$1000[a]	Cost-effectiveness, \$1000/Mg $CHCl_3$
Boise Cascade	St. Helens, OR	739	CEHHD	CEE$_o$DD	1,805	75.8
Lincoln Pulp & Paper	Lincoln, ME	246	CEDD	none	NA	--
Allied Paper	Jackson, AL	454	CEHED	CEDED	1,850	95.9
Champion International	Canton, NC	1,218	CEHED	CEDED	2,246	64.7
Westvaco	Covington, VA	363	CEHD	CE$_o$DD	1,805	96.0
International Paper	Mobile, AL	363	CEDED	none	NA	--
Crown Zellerbach	St. Francisville, LA	450	CEHD	CE$_o$DD	168	8.7
Crown Zellerbach	Clatskanie, OR	760	CEHED	CEDED	1,850	95.9
Union Camp	Franklin, VA	1,770	CEDED	none	NA	--
Kimberly Clark	Coosa Pines, AL	775	CEDED	none	NA	--
Southland Paper Mills	Lufkin, TX	314	CEH	CE$_o$D	2,197	162.7
Bowater Southern	Calhoun, TN	513	CEH	CE$_o$D	2,197	28.6
Alpha Cellulose	Lumberton, NC	64	none	NA	NA	--
Valentine Pulp & Paper	Lockport, LA	90	CEH	CED	1,810	411.4
Hercules, Inc.	Hopewell, VA	218	CEH	CE$_o$D	2,197	305.1
Olin Corp.	Pisgah Forest, NC	80	CEH	CED	1,876	100.3
Southland Paper	Houston, TX	236	CEH	CE$_o$D	2,197	217.5

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[a] Numbers in parentheses represent a net savings.

[b] Calculated from data presented for 181 Mg/day mill in Table 3-12.

[c] Calcuated by interpolating costs for 250 Mg/day mill from data presented in Table 3-12.

[d] Cost represents sum of net savings for three 545 Mg/day model plants.

[e] Cost extrapolated from costs presented in Table 3-12.

TABLE 3-25. SUMMARY OF CHLOROFORM CONTROL COST-EFFECTIVENESS[a]

Subcategory	$1000/Mg Minimum	 Maximum	 Median	 Mean
Market Bleached Kraft	136.0	-0.822	-0.231	24.1
BCT Bleached Kraft	69.7	-0.575	27.6	28.6
Soda and Kraft Fine Bleached	161.5	6.2	70.9	74.0
Papergrade Sulfite	416.9	14.2	62.25	130.6
Miscellaneous Integrated	411.4	-1.4	88.55	102.3
Total, all categories	416.9	-1.4	64.25	85.6

[a] Based on mid-1983 dollars.

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6. The Bleaching of Pulp. Third edition. R.P. Singh, editor. Technical Association of the Pulp and Paper Industry, Inc. Atlanta, Georgia. 1979. p. 5.

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8. Reference 6, p. 6

9. Reference 6, p. 306.

10. Reference 6, p. 3.

11. Letter and attachment from W. Gillespie, National Council for Air and Stream Improvement, New York, NY to S. Duletsky, GCA Corporation. March 11, 1983.

12. Reference 2, p. 10.

13. Reference 3, pp. 179-180.

14. Telephone conversation between S. Duletsky, GCA Corporation and M. Barker, Technical Association of the Pulp and Paper Industry, Atlanta, GA. March 7, 1983.

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16. Reference 6, p. 325.

17. Telephone conversation between S. Duletsky, GCA Corporation and Mr. Prough, KAMYR Co., Glens Falls, NY. March 25, 1983.

18. Telephone conversation between S. Duletsky, GCA Corporation and B. Collins, KAMYR Co., Glens Falls, NY. March 9, 1983.

19. Reference 6, pp. 135-141.

20. Reference 6, pp. 311-313.

21. Letter and attachments from R. Schleinkofer, Impco Division, Ingersoll-Rand Company, Nashua, NH, to S. Duletsky, GCA Corporation, June 30, 1983.

22. Letter and attachments from W. Gillespie, NCASI, New York, NY, to S. Duletsky, GCA Corporation, July 8, 1983.

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4. ETHYLENE DICHLORIDE PRODUCTION

INTRODUCTION

Chloroform is formed as a byproduct during the production of ethylene dichloride (EDC). EDC is produced from ethylene and chlorine by direct chlorination, and ethylene and hydrogen chloride (HCl) by oxychlorination. At most production facilities, where EDC is used on-site to produce vinyl chloride monomer (VCM), these processes are used together in what is known as the balanced process. In the balanced process, byproduct HCl from the cracking of EDC to produce VCM is used in the oxychlorination process to produce about half of the EDC required for VCM production. The remaining EDC is produced by direct chlorination. The balanced process consists of an oxychlorination operation, a direct chlorination operation, and product finishing and waste treatment operation. At EDC production facilities where VCM is not produced, EDC is typically produced by direct chlorination.

There are currently 20 facilities in the United States that produce EDC.[1] Table 4-1 lists the company, location, and annual production capacity for each facility. Figure 4-1 presents plant locations. Five of these facilities produce EDC by direct chlorination; eleven plants use the balanced process with oxygen-based oxychlorination; three plants use the balanced process with air-based oxychlorination process; and one plant manufactures EDC by air-based oxychlorination only (see Tables 4-4 through 4-21). The most recent estimate of domestic EDC production is 5,110 Gg, a preliminary figure for 1983.[2] With the total capacity cited in Table 5-1, the overall EDC capacity utilization for 1983 is about 58 percent.

TABLE 4-1. PRODUCERS OF ETHYLENE DICHLORIDE[1]

Manufacturer	Location	Annual capacity[a] (x 10^3 Mg)
ARCO Chemical Co.	Port Arthur, TX	225
Borden Chemical Co.	Geismar, LA	230
Diamond Shamrock Corp.	Deer Park, TX	85
Dow Chemical U.S.A.	Freeport, TX	725
	Oxyster Creek, TX	550
	Plaquemine, LA	940
E.I. duPont de Nemours & Co., Inc.		
Conoco Chems. Co. Div.	Lake Charles, LA	525
Ethyl Corp.	Baton Rouge, LA	320
	Pasadena, TX	100
Formosa Plastics Corp. U.S.A.	Baton Rouge, LA	250
	Point Comfort, TX	385
Georgia-Pacific Corp.	Plaquemine, LA	750
The BF Goodrich Co.		
BF Goodrich Chem. Group	La Porte, TX	720
Convent Chem. Corp., subsid.	Calvert City, KY	450
	Convent, LA	360
PPG Industries, Inc.	Lake Charles, LA	1,225
Shell Chemical Co.	Deer Park, TX	635
Union Carbide Corp.	Taft, LA	70[b]
	Texas City, TX	70[b]
Vulcan Materials Co.	Geismar, LA	160
		8,775

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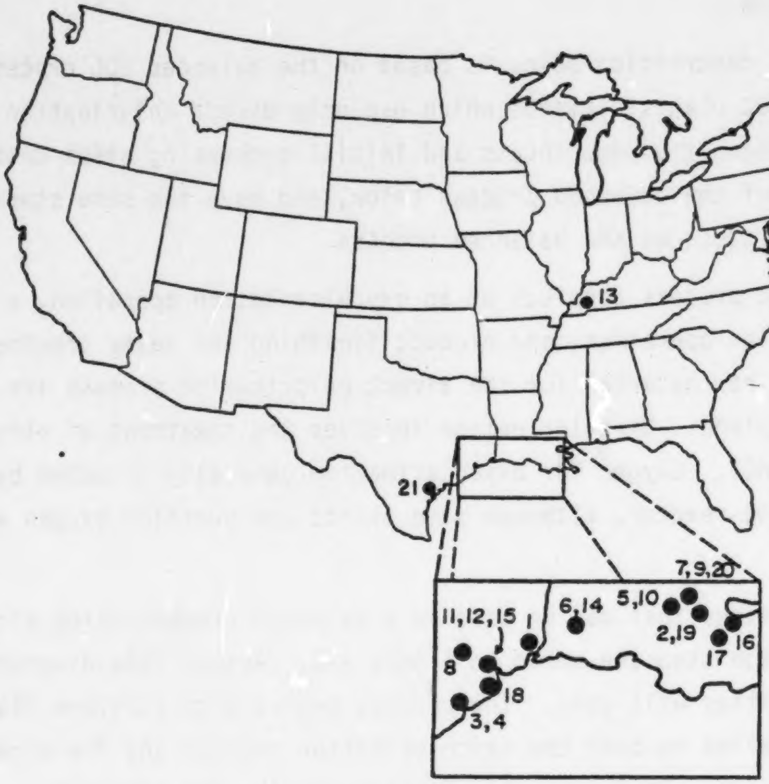
[a] Capacities are flexible depending on finishing capacities for vinyl chloride and chlorinated solvents.

[b] Captive use only.



1. ARCO Chemical Co., Port Arthur, TX
2. Borden Chemical, Geismar, LA
3. Dow Chemical USA, Freeport, TX
4. Dow Chemical USA, Oyster Creek, TX
5. Dow Chemical USA, Plaquemine, LA
6. Conoco Chemicals, Lake Charles, LA
7. Ethyl Corp., Baton Rouge, LA
8. Ethyl Corp., Pasadena, TX
9. Formosa Plastics, Baton Rouge, LA
10. Georgia Pacific Corp., Plaquemine, LA
11. Diamond Shamrock, Deer Park, TX
12. BF Goodrich, La Porte, TX
13. BF Goodrich, Calvert City, KY
14. PPG Industries, Lake Charles, LA
15. Shell Chemical Co., Deer Park, TX
16. Shell Chemical Co., Norco, LA (out of production)
17. Union Carbide Corp., Taft, LA
18. Union Carbide Corp., Texas City, TX
19. Vulcan Chemical, Geismar, LA
20. BF Goodrich/Convent, Convent, LA
21. Formosa Plastics, Point Comfort, TX

Figure 4-1. Locations of ethylene dichloride production facilities.

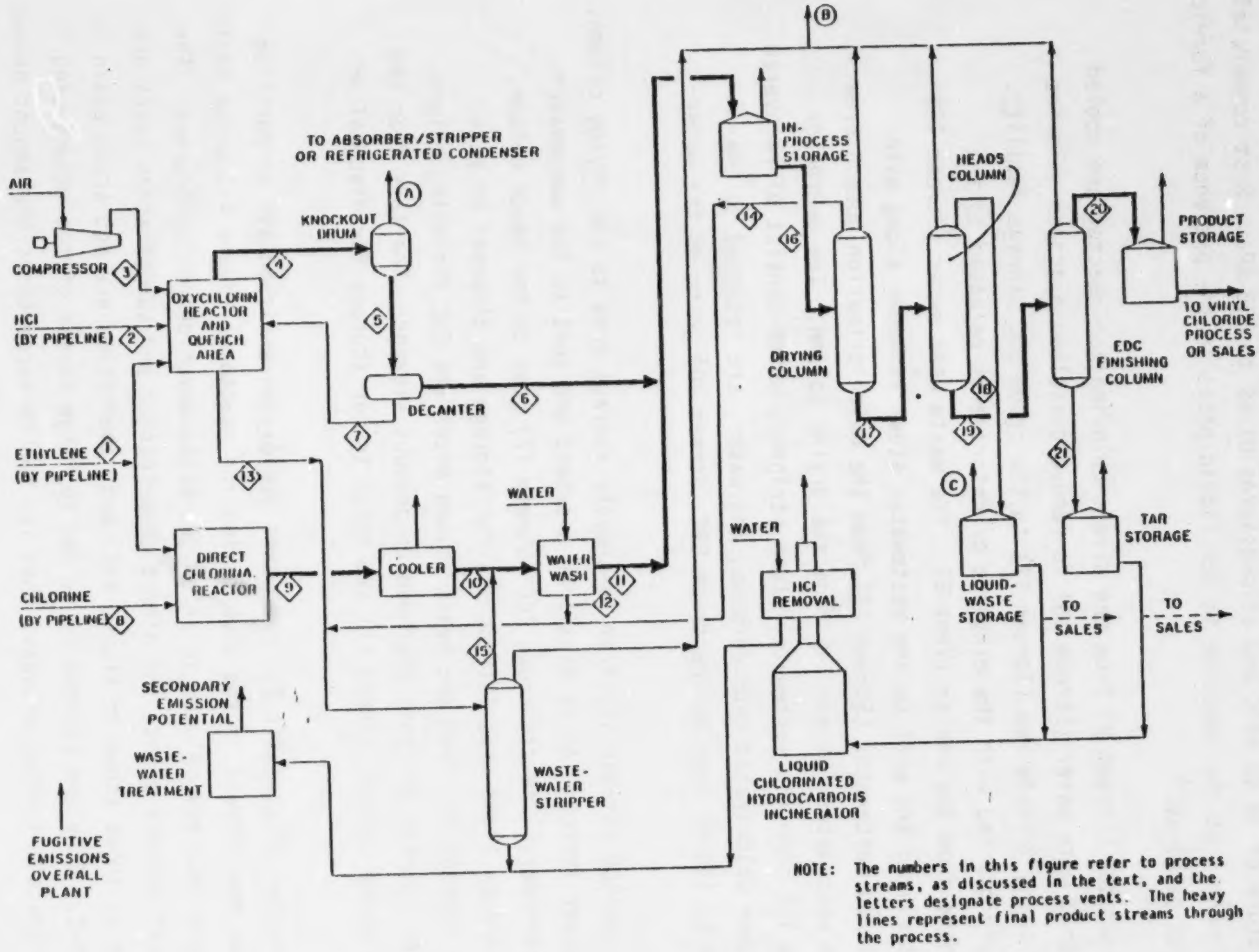
SOURCE DESCRIPTION

The process description below is based on the balanced EDC process, used at all but six EDC plants. Plants which use only direct chlorination or oxychlorination have the same inputs and initial processing steps described for those parts of the balanced process below, and have the same storage and purification steps as the balanced process.

The balanced process consists of an oxychlorination operation, a direct chlorination operation, and product finishing and waste treatment operations. The raw material for the direct chlorination process are chlorine and ethylene. Oxychlorination involves the treatment of ethylene with oxygen and HCl. Oxygen for oxychlorination generally is added by feeding air to the reactor, although some plants use purified oxygen as feed material.[3]

Basic operations that may be used in a balanced process using air for the oxychlorination step are shown in Figure 4-2. Actual flow diagrams for production facilities will vary. The process begins with ethylene (Stream 1) being fed by pipeline to both the oxychlorination reactor and the direct chlorination reactor. In the oxychlorination reactor the ethylene, anhydrous hydrogen chloride (Stream 2), and air (Stream 3) are mixed at molar proportions of about 2:4:1, respectively, producing 2 moles of EDC and 2 moles of water. The reaction is carried out in the vapor phase at 200 to 315°C in either fixed-bed or fluid-bed reactor. A mixture of copper chloride and other chlorides is used as a catalyst.[3]

The products of reaction from the oxychlorination reactor are quenched with water, cooled (Stream 4), and sent to a knockout drum, where EDC and water (Stream 5) are condensed. The condensed stream enters a decanter, where crude EDC is separated from the aqueous phase. The crude EDC (Stream 6) is transferred to in-process storage, and the aqueous phase (Stream 7) is recycled to the quench step. Nitrogen and other inert gases are typically vented to an incinerator, although at some locations this stream is released to the atmosphere (Vent A). The concentration of organics in the vent stream is reduced by absorber and stripper columns or by a refrigerated condenser (not shown in Figure 4-2).[3,4]


TO ABSORBER/STRIPPER OR REFRIGERATED CONDENSER
A
B
C
AIR
COMPRESSOR
3
HCl (BY PIPELINE)
2
ETHYLENE (BY PIPELINE)
1
CHLORINE (BY PIPELINE)
8
OXYCHLORIN REACTOR AND QUENCH AREA
KNOCKOUT DRUM
4
5
DECANTER
6
7
13
DIRECT CHLORINA. REACTOR
9
COOLER
10
WATER
WATER WASH
11
12
15
WASTE-WATER STRIPPER
SECONDARY EMISSION POTENTIAL
WASTE-WATER TREATMENT
FUGITIVE EMISSIONS OVERALL PLANT
IN-PROCESS STORAGE
14
16
DRYING COLUMN
17
HEADS COLUMN
18
19
EDC FINISHING COLUMN
20
21
PRODUCT STORAGE
TO VINYL CHLORIDE PROCESS OR SALES
WATER
HCl REMOVAL
LIQUID CHLORINATED HYDROCARBONS INCINERATOR
LIQUID-WASTE STORAGE
TO SALES
TAR STORAGE
TO SALES

NOTE: The numbers in this figure refer to process streams, as discussed in the text, and the letters designate process vents. The heavy lines represent final product streams through the process.

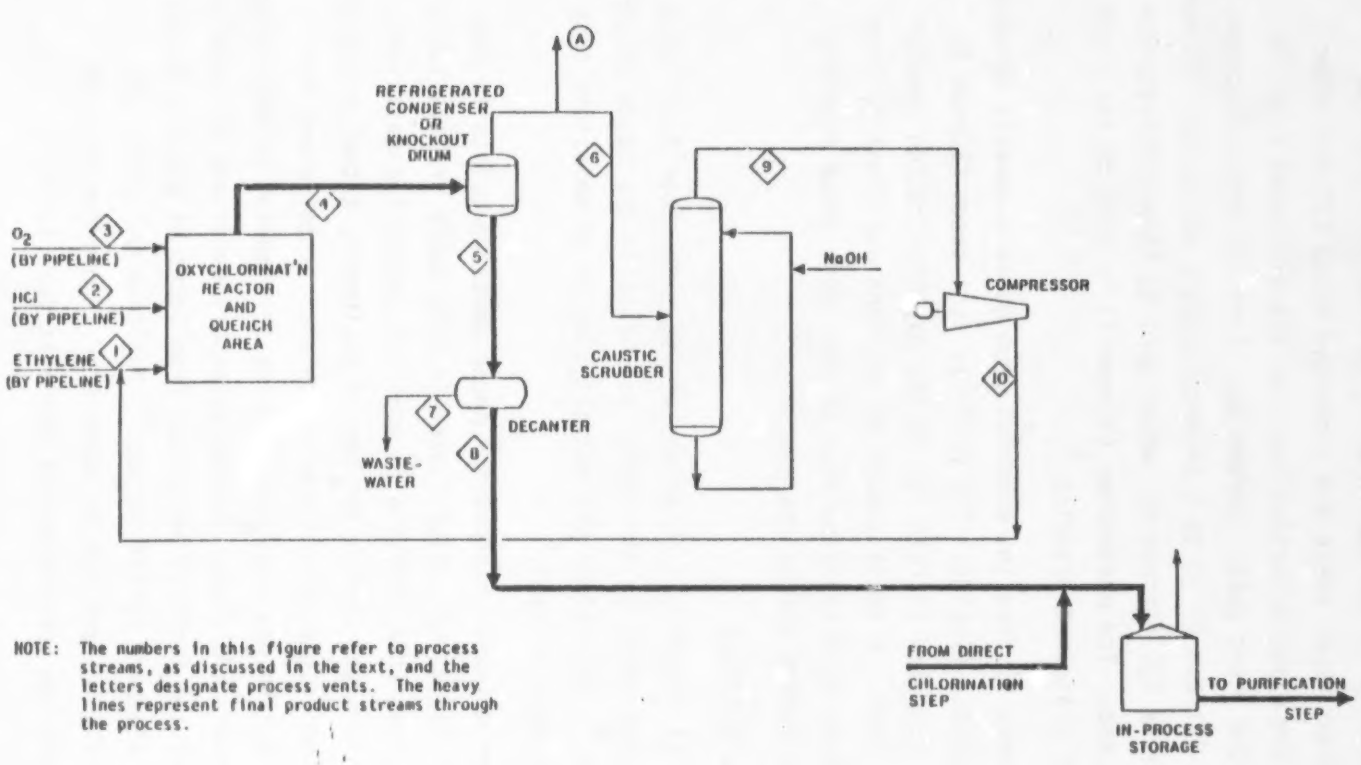
Figure 4-2. Basic operations that may be used in the production of ethylene dichloride by the balanced process, with air-based oxychlorination.3

In the direct-chlorination step of the balanced process, equimolar amounts of ethylene (Stream 1) and chlorine (Stream 8) are reacted at a temperature of 38 to 49°C and at pressures of 69 to 138 kPa. Most commercial plants carry out the reaction in the liquid phase in the presence of a ferric chloride catalyst.[3]

Products (Stream 9) from the direct chlorination reactor are cooled and washed with water (Stream 10) to remove dissolved hydrogen chloride before being transferred (Stream 11) to the crude EDC storage facility. Any inert gas fed with the ethylene or chlorine is released to the atmosphere from the cooler (Vent B). The waste wash water (Stream 12) is neutralized and sent to the wastewater steam stripper along with neutralized wastewater (Stream 13) from the oxychlorination quench area and the wastewater (Stream 14) from the drying column. The overheads (Stream 15) from the wastewater steam stripper, which consist of recovered EDC, other chlorinated hydrocarbons, and water, are returned to the process by adding them to the crude EDC (Stream 10) going to the water wash.[3]

Crude EDC (Stream 16) from in-process storage goes to the drying column, where water (Stream 14) is distilled overhead and sent to the wastewater steam stripper. The dry crude EDC (Stream 17) goes to the heads column, which removes light ends (Stream 18) for storage and disposal or sale. Bottoms (Stream 19) from the heads column enter the EDC finishing column, where EDC (Stream 20) goes overhead to product storage. The tars from the EDC finishing column (Stream 21) are taken to tar storage for disposal or sale.[3]

A number of domestic EDC producers use oxygen-enriched air or purified oxygen as the oxidant in the oxychlorination reactor. Figure 4-3 shows basic operations that may be used in an oxygen-based oxychlorination process. For a balanced process plant, the direct chlorination and purification steps are the same as those shown in Figure 4-2, and, therefore, are not shown again in Figure 4-3. Ethylene (Stream 1) is fed in large excess of the amount used in the air oxychlorination process, that is, two to three times the amount needed


REFRIGERATED CONDENSER OR KNOCKOUT DRUM
A
6
9
4
3
O_2 (BY PIPELINE)
2
HCl (BY PIPELINE)
1
ETHYLENE (BY PIPELINE)
OXYCHLORINAT'N REACTOR AND QUENCH AREA
5
NaOH
COMPRESSOR
CAUSTIC SCRUBBER
10
7
DECANTER
8
WASTE-WATER
FROM DIRECT CHLORINATION STEP
TO PURIFICATION STEP
IN-PROCESS STORAGE

NOTE: The numbers in this figure refer to process streams, as discussed in the text, and the letters designate process vents. The heavy lines represent final product streams through the process.

Figure 4-3. Basic operations that may be used in the production of ethylene dichloride by the balanced process, oxygen-based oxychlorination step.[3]

to fully consume the HCl feed (Stream 2). Oxygen (Stream 3) is also fed to the reactor, which may be either a fixed bed or a fluid bed. After passing through the condensation step in the quench area, the reaction products (Stream 4) go to a knockout drum, where the condensed crude EDC and water (Stream 5) produced by the oxychlorination reaction are separated from the unreacted ethylene and the inert gases (Stream 6). From the knockout drums the crude EDC and water (Stream 5) go to a decanter, where wastewater (Stream 7) is separated from the crude EDC (Stream 8), which goes to in-process storage as in the air-based process. The wastewater (Stream 7) is sent to the steam stripper for recovery of dissolved organics.[3]

The vent gases (Stream 6) from the knockout drum go to a caustic scrubber for removal of HCl and carbon dioxide. The purified vent gases (Stream 9) are then compressed and recycled (Stream 10) to the oxychlorination reactor as part of the ethylene feed. A small amount of the vent gas (Vent A) from the knockout drum is purged to prevent buildup of the inert gases entering with the feed streams or formed during the reaction.[3]

CHLOROFORM EMISSIONS AND CONTROLS

Identified sources of chloroform emissions at EDC production facilities include the oxychlorination vent, column vents, particularly the heads columns, and liquid waste storage.[5] Chloroform was not detected in an emissions test of a direct chlorination reactor vent.[6]

Available chloroform emission factors for these emission points in EDC production are listed in Table 4-2. Also listed in this table are available control techniques and associated emission factors for controlled emissions. Because of variations in process design and age of equipment, actual emissions vary for each plant. Other potential sources of chloroform emissions for which insufficient information was available for the development of chloroform emission factors in a recent EPA study include secondary emissions of chloroform from wastewater treatment and fugitive emissions from leaks in process valves, pumps, compressors, and pressure relief valves.[5] Fugitive emissions are expected to be low or insignificant due to absence of chloroform in some process components and the low concentrations where it does exist.

TABLE 4-2. CONTROLLED AND UNCONTROLLED CHLOROFORM EMISSION FACTORS FOR A HYPOTHETICAL FACILITY PRODUCING ETHYLENE DICHLORIDE[a]

Emission source	Source designation[b]	Uncontrolled chloroform emission factor[c]	Available control technique (ACT)[d]	Percent reduction	Controlled chloroform emission factor[c]
Oxychlorination vent					
Air process	A	0.033 to 0.65 kg/Mg	Thermal oxidizer	98+	$\leq 6.6\text{x}10^{-4}$ to $1.3\text{x}10^{-2}$ kg/Mg
Oxygen process	A	0.0050 to 0.12 kg/Mg	Thermal oxidizer	98+	$\leq 1.0\text{x}10^{-4}$ to $2.4\text{x}10^{-3}$ kg/Mg
Column vents	B	1.0 kg/Mg	Thermal oxidizer	98+	≤0.02 kg/Mg
Liquid waste storage	C	0.003 kg/Mg	Refrigerated condenser	85	$4.5\text{x}10^{-4}$ kg/Mg

[a] Reference 5. Any given EDC production plant may vary in configuration and level of control from this hypothetical facility.

[b] Letters refer to vents designated to Figure 4-2, except for the oxygen-based oxychlorinator vent which is shown in Figure 4-3.

[c] Emission factors in terms of kg/Mg refer to kilogram of chloroform emitted per megagram of EDC produced by the balanced process. In cases where a particular source designation applies to multiple operations, these factors represent combined emissions for all, not each, of these operations within the hypothetical facility. See Reference 5 for emission factor derivations.

[d] The control efficiency for incineration varies depending on the design of the incinerator and the compound which is burned. The 98 percent level is an estimate of the control efficiency of an incinerator with a residence time of about 1 second and a temperature of about 1100°C, for a compound which is difficult to incinerate. Incinerators operating at longer residence times and higher temperatures would achieve higher efficiencies. Refrigerated condenser as control technique for emissions from liquid waste storage and associated reduction of 85% from Reference 3.

Table 4-3 summarizes estimated current chloroform emissions from EDC production facilities. Tables 4-4 through 4-21 provide derivations and sources as well as control information and vent parameters for individual facilities. In this analysis, it was assumed that the oxygen process and thermal oxidation are in use at five facilities in Louisiana which are under negotiated agreements to make these changes to air-based processes by the end of 1984. These plants are Borden/Geismar, Conoco/Lake Charles, Ethyl/Baton Rouge, Formosa Plastics/Baton Rouge, and Vulcan/Geismar. Lack of plant-specific information on liquid waste disposal or storage and other potential chloroform emission points made estimation of their emissions impossible. The emission estimates presented here are based on average uncontrolled emission factors of 0.35 kg/Mg for air process vents, and 0.06 for oxygen process vents, and a thermal oxidizer control efficiency of 98 percent, unless noted otherwise in Tables 4-4 through 4-21. Production rates were estimated using the capacities cited in Table 4-1 assuming that each plant is operating at the 58 percent national average capacity utilization cited earlier. Unless noted, vent parameters are from a previous study.[3]

Chloroform emissions from the Union Carbide facilities in Texas City, Texas and Taft, Louisiana were assumed to be negligible. Both of these plants produce EDC by direct chlorination for captive use with an annual production capacity of 70,000 Mg. The plant in Texas City vents emissions from EDC production to a flare and the controlled emissions contain no measurable chloroform.[7] Information on the plant in Taft was not available; however, based on the general similarities between the two Union Carbide facilities, no chloroform was assumed to be emitted from the Taft plant.

Available control techniques (ACT) consist of thermal incineration at 98 percent except where higher current control efficiencies have been reported. For plants where current control is thermal oxidation, Tables 4-4 through 4-21 contain one entry which represents both current and ACT emissions. Where current emissions are below those achievable by ACT, both are estimated.

TABLE 4-3. ESTIMATED CHLOROFORM EMISSIONS FROM ETHYLENE DICHLORIDE PRODUCTION FACILITIES

Manufacturer	Location	Current chloroform emissions (kg/yr)	Available control technique emissions (kg/yr)
ARCO	Port Arthur, TX	2,600	2,600
Borden	Geismar, LA	2,800	2,800
Diamond Shamrock	Deer Park, TX	53,600	1,300
Dow	Freeport, TX	9,000	9,000
Dow	Oyster Creek, TX	6,800	6,800
Dow	Plaquemine, LA	11,600	11,600
DuPont	Lake Charles, LA	6,500	6,500
Ethyl	Baton Rouge, LA	3,900	3,900
Ethyl	Pasadena, TX	1,160	1,160
Formosa Plastics	Baton Rouge, LA	3,100	3,100
Formosa Plastics	Point Comfort, TX	4,730	4,730
Georgia Pacific	Plaquemine, LA	9,200	9,200
B.F. Goodrich	LaPorte, TX	570	570
B.F. Goodrich	Calvert City, KY	10,720	7,050
B.F. Goodrich	Convent, LA	4,180	4,180
PPG	Lake Charles, LA	15,100	15,100
Shell	Deer Park, TX	7,800	7,800
Vulcan	Geismar, LA	19,820	19,820
TOTAL		173,180	117,210

TABLE 4-4. EMISSION SUMMARY FOR ARCO POLYMER/PORT ARTHUR, TX

Company: ARCO Polymer
Location: Port Arthur, TX
Production Process: Direct chlorination[a]
Production Rate: 130,000 Mg/yr
Latitude: 29° 52' 00" Longitude: 93° 59' 45"

Source	Control technique[a]	Chloroform emission rate (kg/yr)	Vent height (m)	Vent diameter (m)	Discharge temp. (°K)	Discharge velocity (m/sec)
Column vents	Thermal oxidizer	2,600	30	0.73	340	14

[a] Information on process and control techniques from Reference 8.

TABLE 4-5. EMISSION SUMMARY FOR BORDEN/GEISMAR, LA

Company: Borden
Location: Geismar, LA
Production Process: Balanced with oxygen-based oxychlorination[a]
Production Rate: 133,000 Mg/yr
Latitude: 30° 12' 20" Longitude: 91° 01' 08"

Source	Control technique[a]	Chloroform emission rate (kg/yr)	Vent height (m)	Vent diameter (m)	Discharge temp. (°K)	Discharge velocity (m/sec)
Oxychlorinator vent and column vents	Thermal oxidizer	2,800	30	1.0	340	13

[a] Information on process and control techniques from Reference 9.

TABLE 4-6. EMISSION SUMMARY FOR DIAMOND SHAMROCK/DEER PARK, TX

Company: Diamond Shamrock
Location: Deer Park, TX
Production Process: Balanced with air-based oxychlorination[a]
Production Rate: 49,300 Mg/yr
Latitude: 29° 44' 01" Longitude: 95° 06' 44"

Source	Control technique[a]	Chloroform emission rate (kg/yr)	Vent height (m)	Vent diameter (m)	Discharge temp. (°K)	Discharge velocity (m/sec)
CURRENT EMISSIONS						
Oxychlorinator vents	Catalytic oxidizer	4,300	30	0.61	340	14
Column vents	None	49,300	20	0.2	300	6.9
AVAILARLE CONTROL TECHNIQUE EMISSIONS						
Oxychlorinator and column vents	Thermal oxidizer	1,300	30	1.1	340	14

[a] Information on process, control techniques from Reference 9.

[b] Catalytic oxidizer control efficiency of 75 percent for chloroform assumed from efficiency cited for EDC in Reference 10; vent parameters assumed to be the same as thermal oxidizer.

TABLE 4-7. EMISSION SUMMARY FOR DOW/FREEPORT, TX

Company: Dow
Location: Freeport, TX
Production Process: Balanced with oxygen-based oxychlorination[a]
Production Rate: 430,000 Mg/yr
Latitude: 29° 02' 00" Longitude: 95° 13' 00"

Source	Control technique[a]	Chloroform emission rate (kg/yr)	Vent height (m)	Vent diameter (m)	Discharge temp. (°K)	Discharge velocity (m/sec)
Oxychlorinator vent and column vents	Thermal oxidizer	9,000	30	1.0	340	13

[a] Information on process and control techniques from Reference 9.

TABLE 4-8. EMISSION SUMMARY FOR DOW/OYSTER CREEK, TX

Company: Dow
Location: Oyster Creek, TX
Production Process: Balanced with oxygen-based oxychlorination[a]
Production Rate: 319,000 Mg/yr
Latitude: 28° 51' 27" Longitude: 95° 20' 90"

Source	Control technique[a]	Chloroform emission rate (kg/yr)	Vent height (m)	Vent diameter (m)	Discharge temp. (°K)	Discharge velocity (m/sec)
Oxychlorinator vent and column vents	Thermal oxidizer	6,800	30	1.0	340	13

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[a] Information on process and control techniques is from Reference 9.

TABLE 4-9. EMISSION SUMMARY FOR DOW/PLAQUEMINE, LA

Company: Dow
Location: Plaquemine, LA
Production Process: Balanced with oxygen-based oxychlorination[a]
Production Rate: 545,000 Mg/yr
Latitude: 30° 19' 21" Longitude: 91° 14' 39"

Source	Control technique[a]	Chloroform emission rate (kg/yr)	Vent height (m)	Vent diameter (m)	Discharge temp. (°K)	Discharge velocity (m/sec)
Oxychlorinator vent and column vents	Thermal oxidizer	11,600	30	1.0	340	13

[a] Information on process and control techniques from Reference 6.

TABLE 4-10. EMISSION SUMMARY FOR DUPONT/CONOCO CHEMICAL/LAKE CHARLES, LA

Company: DuPont/Conoco Chemical
Location: Lake Charles, LA
Production Process: Balanced with oxygen-based oxychlorination[a]
Production Rate: 305,000 Mg/yr
Latitude: 30° 15' 09" Longitude: 93° 17' 05"

Source	Control technique[a]	Chloroform emission rate (kg/yr)	Vent height (m)	Vent diameter (m)	Discharge temp. (°K)	Discharge velocity (m/sec)
Oxychlorinator vent and column vents	Thermal oxidizer	6,500	30	1.0	340	13

[a] Information on process and control techniques from References 11 and 12.

TABLE 4-11. ETHYL CORP./BATON ROUGE, LA

Company: Ethyl Corp.
Location: Baton Rouge, LA
Production Process: Balanced with oxygen-based oxychlorination[a]
Production Rate: 185,600 Mg
Latitude: 30° 29' 49" Longitude: 91° 10' 50"

Source	Control technique[a]	Chloroform emission rate (kg/yr)	Vent height (m)	Vent diameter (m)	Discharge temp. (°K)	Discharge velocity (m/sec)
Oxychlorinator vent and column vents	Thermal oxidizer	3,900	30	1.0	340	13

[a] Process and control information from Reference 13.

TABLE 4-12. EMISSION SUMMARY FOR ETHYL CORP./PASADENA, TX

Company: Ethyl Corp.
Location: Pasadena, TX
Production Process: Direct chlorination
Production Rate: 58,000 Mg/yr
Latitude: 29° 44' 21" Longitude: 95° 10' 03"

Source	Control technique	Chloroform emission rate (kg/yr)	Vent height (m)	Vent diameter (m)	Discharge temp. (°K)	Discharge velocity (m/sec)
Column vents	Incineration in lead furnaces[a]	1,160	30	0.73	340	14

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[a] Incineration of uncondensed vent gases in "lead furnaces"[14] assumed equivalent to thermal oxidizer.

TABLE 4-13. EMISSION SUMMARY FOR FORMOSA PLASTICS/BATON ROUGE, LA

Company: Formosa Plastics
Location: Baton Rouge, LA
Production Process: Balanced with oxygen-based oxychlorination
Production Rate: 145,000 Mg/yr
Latitude: 30° 21' 40" Longitude: 91° 11' 35"

Source	Control technique	Chloroform emission rate (kg/yr)	Vent height (m)	Vent diameter (m)	Discharge temp. (°K)	Discharge velocity (m/sec)
Oxychlorinator vent and column vents	Thermal oxidizer[a]	3,100	30	1.0	340	13

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[a] Reported incinerator efficiency of 99.99 percent[15] applied to vent emission factors.

TABLE 4-14. EMISSION SUMMARY FOR FORMOSA PLASTICS/POINT COMFORT, TX

Company: Formosa Plastics
Location: Point Comfort, TX
Production Process: Oxygen-based oxychlorination[a]
Production Rate: 223,000 Mg/yr
Latitude: 28° 41' 04" Longitude: 96° 32' 21"

Source	Control technique	Chloroform emission rate (kg/yr)	Vent height (m)	Vent diameter (m)	Discharge temp. (°K)	Discharge velocity (m/sec)
Oxychlorinator vent and column vents	Thermal oxidizer[a]	2,365 2,365	36 36	0.6 0.6	320 320	13 13

---

[a] Information on process, controls and vent parameters from Reference 15, except for model plant emissions and discharge velocity.

TABLE 4-15. EMISSION SUMMARY FOR GEORGIA PACIFIC, PLAQUEMINE, LA

Company: Georgia Pacific
Location: Plaquemine, LA
Production Process: Balanced with oxygen-based oxychlorination[a]
Production Rate: 435,000 Mg/yr
Latitude: 30° 15' 52" Longitude: 91° 11' 06"

Source	Control technique[a]	Chloroform emission rate (kg/yr)	Vent height (m)	Vent diameter (m)	Discharge temp. (°K)	Discharge velocity (m/sec)
Oxychlorinator vent and column vents	Thermal oxidizer	9,200	30	1.0	340	13

---

[a] Information on process and control techniques from Reference 16.

TABLE 4-16. EMISSION SUMMARY FOR B.F. GOODRICH/LA PORTE, TX

Company: B.F. Goodrich
Location: La Porte, TX
Production Process: Balanced with air-based oxychlorination[a]
Production Rate: 418,000 Mg/yr
Latitude: 29° 44' 39" Longitude: 95° 04' 35"

Source	Control technique	Chloroform emission rate (kg/yr)	Vent height (m)	Vent diameter (m)	Discharge temp. (°K)	Discharge velocity (m/sec)
Oxychlorinator vent and column vents	Thermal oxidizer[a]	570	30	1.1	340	14

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[a] Information on process and control techniques from Reference 9, control efficiency (99.9 percent) from Reference 17.

TABLE 4-17. EMISSION SUMMARY FOR B.F. GOODRICH/CALVERT CITY, KY

Company: B.F. Goodrich
Location: Calvert City, KY
Production Process: Balanced with air-based oxychlorination
Production Rate: 261,000 Mg/yr
Latitude: 37° 03' 05" Longitude: 88° 19' 03"

Source	Control technique	Chloroform emission rate (kg/yr)	Vent height (m)	Vent diameter (m)	Discharge temp. (°K)	Discharge velocity (m/sec)
CURRENT EMISSIONS						
Oxychlorinator vents[a]	Thermal oxidation on one vent; absorber on the other (90 percent)	5,500	30	1.0	340	14
Column vents[a]	Thermal oxidation	5,220	30	0.73	340	14
AVAILABLE CONTROL TECHNIQUE EMISSIONS						
Oxychlorinator vents and column vents	Thermal oxidation	7,050	30	1.1	340	14

[a] Control assumptions based on information from Reference 17. Emissions estimated assuming equal division of emission factor-based uncontrolled emissions between two oxychlorination vents. Vent parameters assumed equivalent to thermal oxidizer.

TABLE 4-18. EMISSION SUMMARY FOR B.F. GOODRICH/CONVENT, LA

Company: B.F. Goodrich
Location: Convent, LA
Production Process: Direct chlorination[a]
Production Rate: 209,000 Mg/yr
Latitude: 30° 03' 44" Longitude: 90° 49' 55"

Source	Control technique	Chloroform emission rate (kg/yr)	Vent height (m)	Vent diameter (m)	Discharge temp. (°K)	Discharge velocity (m/sec)
Column vents	Thermal oxidizer[a]	4,180	30	0.73	340	14

[a] Reference 17.

TABLE 4-19. EMISSION SUMMARY FOR PPG/LAKE CHARLES, LA

Company: PPG
Location: Lake Charles, LA
Production Process: Balanced with oxygen-based oxychlorination[a]
Production Rate: 710,000 Mg/yr
Latitude: 30° 13' 28" Longitude: 93° 15' 57"

Source	Control technique[a]	Chloroform emission rate (kg/yr)	Vent height (m)	Vent diameter (m)	Discharge temp. (°K)	Discharge velocity (m/sec)
Oxychlorination vent and column vents	Thermal oxidizer	15,100	30	1.0	340	13

---

[a] Information on process and control techniques from Reference 9.

TABLE 4-20. EMISSION SUMMARY FOR SHELL/DEER PARK, TX

Company: Shell
Location: Deer Park, TX
Production Process: Balanced with oxygen-based oxychlorination[a]
Production Rate: 368,000 Mg/yr
Latitude: 29° 43' 20" Longitude: 95° 07' 80"

Source	Control technique[a]	Chloroform emission rate (kg/yr)	Vent height (m)	Vent diameter (m)	Discharge temp. (°K)	Discharge velocity (m/sec)
Oxychlorinator vent and column vents	Thermal oxidizer	7,800	30	1.0	340	13

[a] Information on process and control technique from Reference 18.

TABLE 4-21. EMISSION SUMMARY FOR VULCAN, GEISMAR, LA

Company: Vulcan
Location: Geismar, LA
Production Process: Oxygen-based oxychlorination
Production Rate: 93,000 Mg/yr
Latitude: 30° 10' 38" Longitude: 90° 57' 21"

Source[a]	Control technique	Chloroform emission rate (kg/yr)	Vent height (m)	Vent diameter (m)	Discharge temp. (°K)	Discharge velocity (m/sec)
Oxychlorinator vent[b]	Thermal oxidizer	20	30	0.61	340	13
Acid scrubber	None	10,000	18	0.15	333	--
Light ends storage	None	3,400	0	0.049	300	--
Hex incinerator	None	6,400	18	0.5	340	12
Wastewater stripper[c]	--	--	--	--	--	--

[a] Sources, controls and vent parameters from Reference 19, except for emissions and vent parameters for oxychlorinator vent, based on emission factor, 98 percent control efficiency and model plant vent parameters.

[b] Reference 20 reports chlorinated hydrocarbon emissions for oxidizer down-time, which will include additional chloroform.

[c] May include some EDC process wastewater chloroform emissions, but is assumed to be mostly due to the chloroform production process at this location (see Chapter 5).

CONCLUSIONS

Costs and cost-effectiveness figures were not calculated for EDC production due to the high level of current control in the industry and unavailability of plant specific data for the few less-controlled plants. As shown in Table 5-3, available information on current controls and emissions indicates that all but two EDC plants are currently controlled at the level considered available control techniques (ACT) in this study. These two plants, Diamond Shamrock/Deer Park, TX and B.F. Goodrich/Calvert City, KY, are estimated to account for 38 percent of current national chloroform emissions from EDC production, with the majority of these emissions due to column vents at the Diamond Shamrock facility, which were assumed to be essentially uncontrolled. Application of ACT at these plants would result in a 33 percent decrease over the current total.

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2. U.S. International Trade Commission. Preliminary Report on U.S. Production of Selected Synthetic Organic Chemicals--Preliminary Totals, 1983. S.O.C. Series C/P-84-1. Washington, DC. March 15, 1984.

3. U.S. Environmental Protection Agency. Organic Chemical Manufacturing Volume 8: Selected Processes. Report 1: Ethylene Dichloride. EPA-450/3-80-028c. Office of Air Quality Planning and Standards. Research Triangle Park, North Carolina. December 1980.

4. Telephone conversation between G. Gasperecz, Louisiana Air Quality Division, Baton Rouge, LA, and M.E. Anderson, GCA/Technology Division. August 5, 1983.

5. Anderson, M.E., and W.H. Battye. Locating and Estimating Air Emissions from Sources of Chloroform, Final Report. U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Research Triangle Park, NC. Contract No. 68-02-3510, Work Assignment No. 22. March 1984.

6. Telephone conversation between G. Gasperecz, Louisiana Air Quality Division, Baton Rouge, LA, and M.E. Anderson, GCA/Technology Division. November 18, 1982.

7. Texas Air Control Board. Emission Inventory Questionnaire for Union Carbide Corp., Texas City, TX. 1976.

8. Texas Air Control Board. Report on Annual SIP Investigation of ARCO Polymers, Inc. June 23, 1982.

9. Reference 3. pp. F-2 and F-3.

10. Reference 3. p. V-3.

11. Letter from J.A. DeBernardi, Conoco Chemicals to D.R. Goodwin, Emissions Standards and Engineering Division, U.S. Environmental Protection Agency. May 16, 1978.

12. Letter from J.A. DeBernardi, Conoco Chemicals to G. VonBodungen, Louisiana Department of Natural Resources concerning hydrocarbon compliance status. July 8, 1981.

13. Letter from N.E. Garland, Ethyl Corp., Baton Rouge, LA, to J.R. Farmer, Emissions Standards and Engineering Division, U.S. Environmental Protection Agency. March 23, 1984.

14. Texas Air Control Board. Report of Annual Compliance Investigation of Ethyl Corporation, Pasadena, Harris County, Texas. June 26, 1979.

15. Telephone conversation between D.A. Beck, Emission Standards and Engineering Division, U.S. Environmental Protection Agency, and Larry Peyton, Formosa Plastics Corp. USA, Point Comfort, TX. July 10, 1984.

16. Memo from Chris Roberie, Air Quality Specialist to G. VonBodungen, Program Administrator, Air Quality Division, Louisiana Department of Natural Resources concerning inspection of Georgia Pacific, Rebecca Plant. March 30, 1981.

17. Letter from W.C. Holbrook, B.F. Goodrich Co., Cleveland, OH, to J.R. Farmer, Emissions Standards and Engineering Division, U.S. Environmental Protection Agency. April 16, 1984.

18. Texas Air Control Board. Report of Annual Compliance Invesigation of Shell Chemical Company, Deer Park, Harris County, Texas. November 10, 1980.

19. Letter and accompanying Emission Inventory Questionnaires from J.W. Bosky, Vulcan Chemicals, Geismar, LA, to G. VonBodungen, Louisiana Department of Natural Resources, Baton Rouge, LA. June 6, 1983.

20. Letter and accompanying Emission Inventory Questionnaires from J.W. Bosky, Vulcan Chemicals, Geismar, LA, to G. VonBodungen, Louisiana Department of Natural Resources, Baton Rouge, LA. June 28, 1983.

5. CHLOROFORM PRODUCTION

INTRODUCTION

Chloroform is produced by hydrochlorination of methanol feedstock, and further chlorination of the resulting methyl chloride intermediate product to produce chloroform and other chloromethanes. As shown in Table 5-1, all of the chloroform production facilities in the U.S. use this basic process. One plant also produces chloroform by methane chlorination. These two processes are discussed in the first section below, followed by description of available information on chloroform emissions, emission controls and control costs.

Figure 5-1 indicates the locations of chloroform production facilities. As indicated in Table 5-1, one of the seven chloroform production facilities (Stauffer/Louisville, KY) is currently on standby. The total production capacity of the seven plants is 234,000 Mg/yr, including Stauffer.[1] The most recent annual chloroform production figure is 159,500 Mg, a preliminary total for 1983.[2] It has been reported that DuPont plans a late-1985 completion date for a new chloroform production unit in Corpus Christi, Texas, with an annual production capacity of 136,400 Mg.[3]

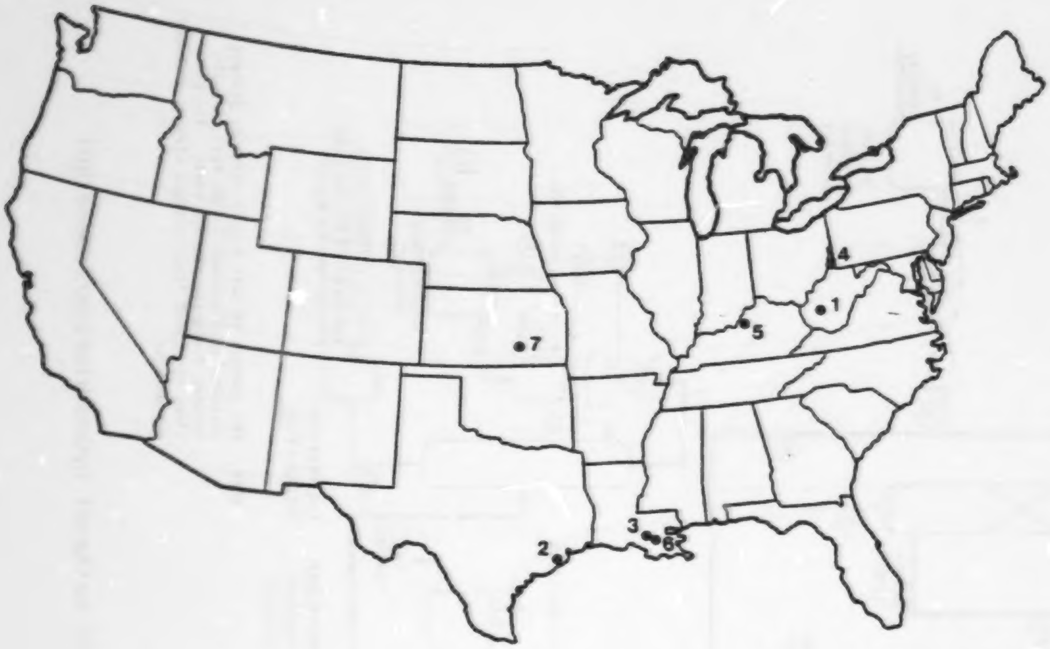
SOURCE DESCRIPTION

The following descriptions of chloroform production processes are based on EPA studies which presented configurations for hypothetical typical plants.[4,5] Individual plants may vary in design and operation. Stream numbers cited in the text refer to Figures 5-2 and 5-3.

TABLE 5-1. CHLOROFORM PRODUCTION FACILITIES[1]

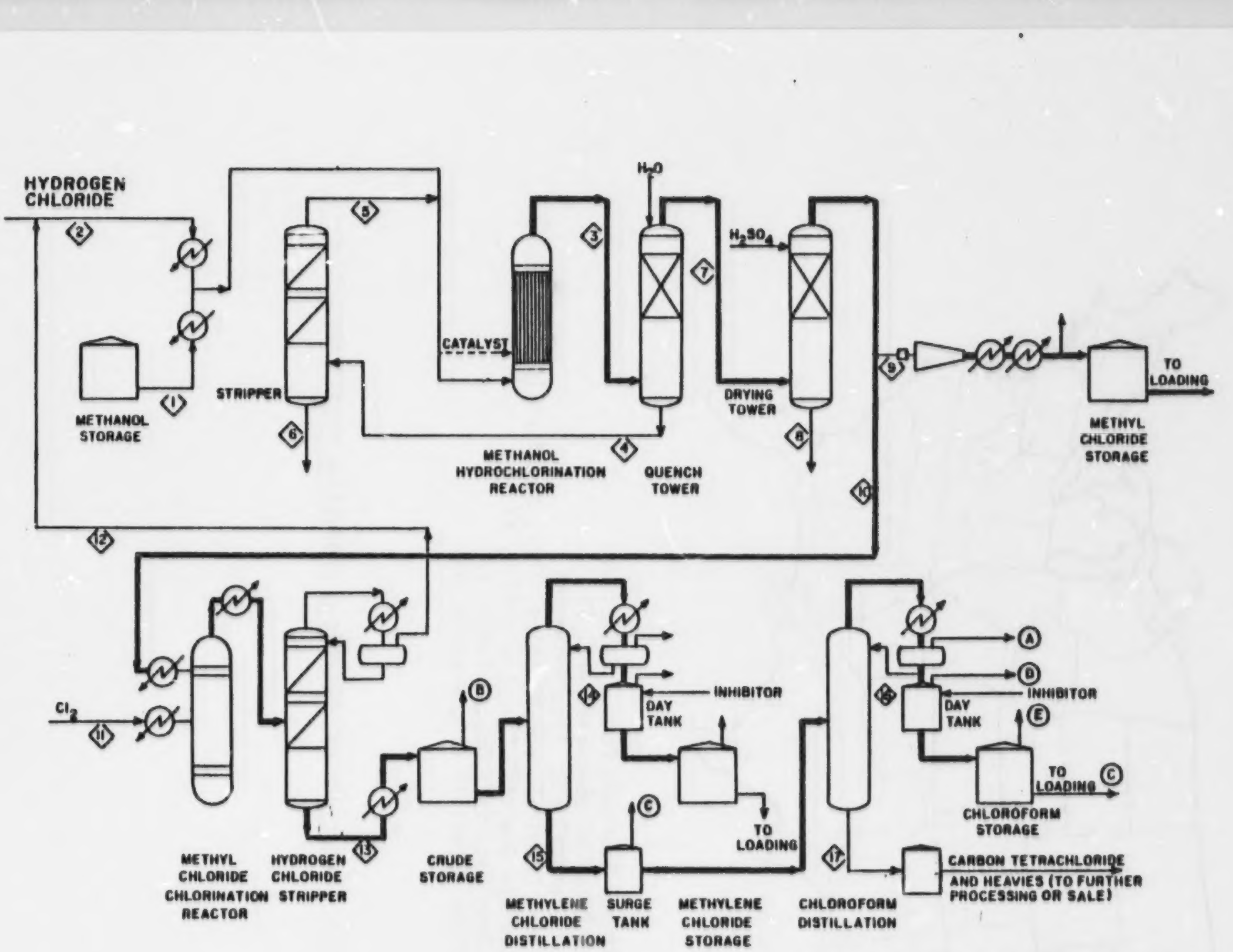
Company	Location	Chloroform capacity (x 10^3 Mg)	Production process
Diamond Shamrock Corp.	Belle, WV	16	Methyl chloride chlorination
Dow Chemical	Freeport, TX	45	Methyl chloride chlorination
	Plaquemine, LA	45	Methyl chloride chlorination
Linden Chemicals and Plastics, Inc.	Moundsville, WV	18	Methyl chloride chlorination
Stauffer Chemical Co.[a]	Louisville, KY	33	Methyl chloride chlorination
Vulcan Materials Co.	Geismar, LA	27	Methyl chloride chlorination
	Wichita, KS	50	67% Methyl chloride chlorination 33% Methane chlorination

[a] Reported to be permanently closed.[28]



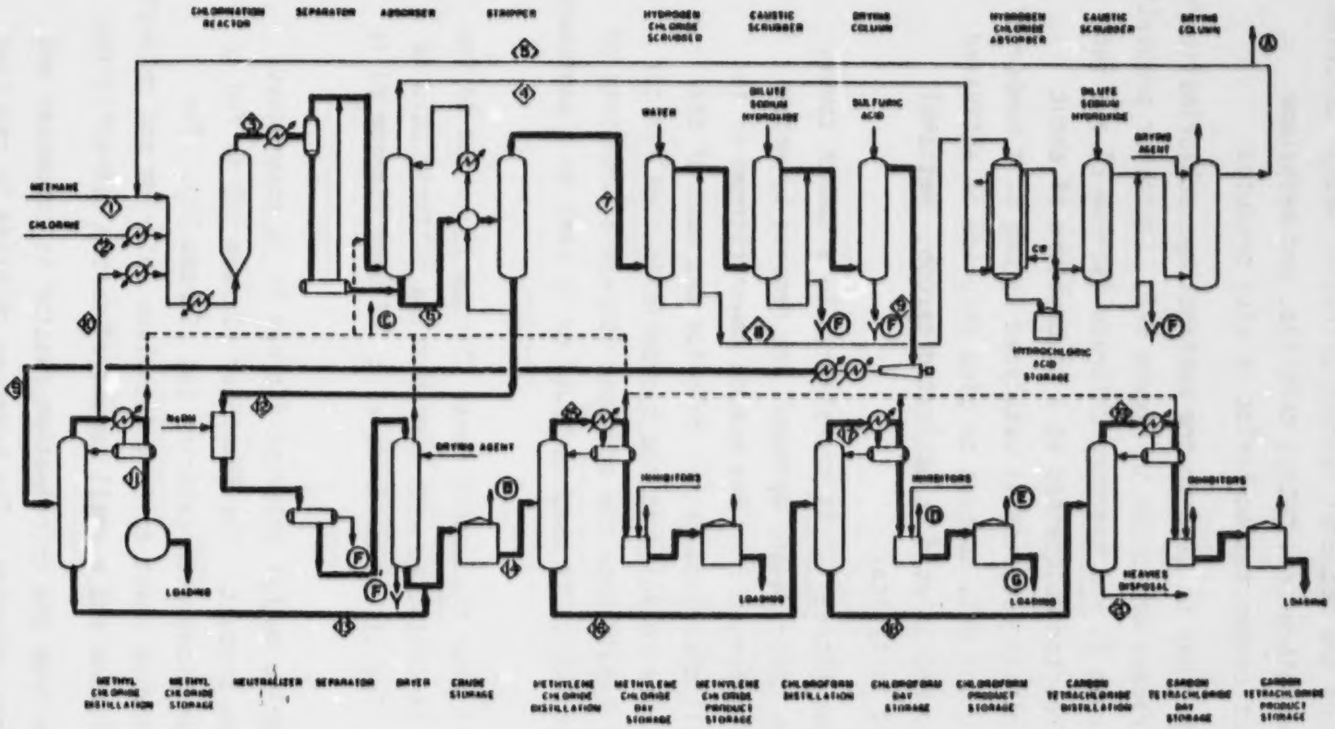
1. Diamond Shamrock Corp., Belle, WV
2. Dow Chemical USA, Freeport, TX
3. Dow Chemical USA, Plaquemine, LA
4. Linden Chemicals and Plastics, Inc., Moundsville, WV
5. Stauffer Chemical Co., Louisville, KY
6. Vulcan Materials Co., Geismar, LA
7. Vulcan Materials Co., Wichita, KS

Figure 5-1. Locations of chloroform production facilities.


HYDROGEN CHLORIDE
2
METHANOL STORAGE
1
STRIPPER
5
6
CATALYST
METHANOL HYDROCHLORINATION REACTOR
3
H_2O
QUENCH TOWER
4
7
H_2SO_4
DRYING TOWER
8
9
10
TO LOADING
METHYL CHLORIDE STORAGE
12
Cl_2
11
METHYL CHLORIDE CHLORINATION REACTOR
HYDROGEN CHLORIDE STRIPPER
13
B
CRUDE STORAGE
14
INHIBITOR
DAY TANK
C
15
METHYLENE CHLORIDE DISTILLATION
SURGE TANK
METHYLENE CHLORIDE STORAGE
TO LOADING
16
A
B
INHIBITOR
DAY TANK
E
TO LOADING
C
CHLOROFORM STORAGE
17
CHLOROFORM DISTILLATION
CARBON TETRACHLORIDE AND HEAVIES (TO FURTHER PROCESSING OR SALE)

NOTE: The numbers in this figure refer to process streams, as discussed in the text, and the letters designate process vents. The heavy lines represent final product streams through the process.

Figure 5-2. Basic operations that may be used in the methanol hydrochlorination/methyl chloride chlorination process.[4]


CHLORINATION REACTOR
SEPARATOR
ABSORBER
STRIPPER
HYDROGEN CHLORIDE SCRUBBER
CAUSTIC SCRUBBER
DRYING COLUMN
HYDROGEN CHLORIDE ABSORBER
CAUSTIC SCRUBBER
DRYING COLUMN
A
METHANE
CHLORINE
WATER
DILUTE SODIUM HYDROXIDE
SULFURIC ACID
DILUTE SODIUM HYDROXIDE
DRYING AGENT
CW
HYDROCHLORIC ACID STORAGE
F
C
NaOH
DRYING AGENT
INHIBITORS
INHIBITORS
INHIBITORS
B
D
E
G
LOADING
LOADING
LOADING
LOADING
HEAVIES DISPOSAL
METHYL CHLORIDE DISTILLATION
METHYL CHLORIDE STORAGE
NEUTRALIZER
SEPARATOR
DRYER
CRUDE STORAGE
METHYLENE CHLORIDE DISTILLATION
METHYLENE CHLORIDE DAY STORAGE
METHYLENE CHLORIDE PRODUCT STORAGE
CHLOROFORM DISTILLATION
CHLOROFORM DAY STORAGE
CHLOROFORM PRODUCT STORAGE
CARBON TETRACHLORIDE DISTILLATION
CARBON TETRACHLORIDE DAY STORAGE
CARBON TETRACHLORIDE PRODUCT STORAGE

NOTE: The numbers in this figure refer to process streams, as discussed in the text, and the letters designate process vents. The heavy lines represent final product streams through the process.

Figure 5-3. Basic operations that may be used in the methane chlorination process.[5]

Methanol Hydrochlorination/Methyl Chloride Chlorination Process[4]

The major products of the methanol hydrochlorination/methyl chloride chlorination process are chloroform, methyl chloride, and methylene chloride. Some byproduct carbon tetrachloride is also produced.

Basic operations that may be used in the methanol hydrochlorination/methyl chloride chlorination process are shown in Figure 5-2. Equimolar proportions of gaseous methanol (Stream 1) and hydrogen chloride (Stream 2) are fed to a hydrochlorination reactor maintained at a temperature of about 350°C. The hydrochlorination reaction is catalyzed by one of a number of catalysts, including alumina gel, cuprous or zinc chloride on activated carbon or pumice, or phosphoric acid on activated carbon. Methanol conversion of 95 percent is typical.

The reactor exit gas (Stream 3) is transferred to a quench tower, where unreacted hydrogen chloride and methanol are removed by water scrubbing. The water discharged from the quench tower (Stream 4) is stripped of virtually all dissolved methyl chloride and most of the methanol, both of which are recycled to the hydrochlorination reactor (Stream 5). The outlet liquid from the stripper (Stream 6) consists of dilute hydrochloric acid, which is used in-house or is sent to a wastewater treatment system.

Methyl chloride gas from the quench tower (Stream 7) is fed to the drying tower, where it is contacted with concentrated sulfuric acid to remove residual water. The dilute sulfuric acid effluent (Stream 8) is sold or reprocessed.

A portion of the dried methyl chloride (Stream 9) is compressed, cooled, and liquefied as product. The remainder (Stream 10) is fed to the chlorination reactor along with chlorine gas (Stream 11). The methyl chloride and chlorine react to form methylene chloride and chloroform, along with hydrogen chloride and a small amount of carbon tetrachloride.

The product stream from the chlorination reactor is condensed and then stripped of hydrogen chloride. The hydrogen chloride is recycled to the methanol hydrochlorination reactor (Stream 12). The crude mixture of methylene chloride, chloroform, and carbon tetrachloride from the stripper (Stream 13) is transferred to a storage tank and then fed to a distillation column to extract methylene chloride. Bottoms from this column (Stream 15) are distilled to extract chloroform. The chloroform and methylene chloride product streams (Streams 14 and 16) are fed to day tanks where inhibitors are added and then sent to storage and loading facilities. Bottoms from chloroform distillation (Stream 17) consist of crude carbon tetrachloride, which is stored for subsequent sale or transferred to a separate carbon tetrachloride/perchloroethylene process.

Methane Chlorination Process[5]

In the methane chlorination process, chloroform is produced as a coproduct with methyl chloride, methylene chloride, and carbon tetrachloride. Methane can be chlorinated thermally, photochemically, or catalytically, with thermal chlorination being the most commonly used method.

Figure 5-3 presents basic operations that may be used in the methane chlorination process. Methane (Stream 1) and chlorine (Stream 2) are mixed and fed to a chlorination reactor, which is operated at a temperature of about 400°C and a pressure of about 200 kPa.[5] Gases exiting the reactor (Stream 3) are partly condensed and then scrubbed with chilled crude product to absorb most of the product chloromethanes from the unreacted methane and byproduct hydrogen chloride. The unreacted methane and byproduct hydrogen chloride from the absorber (Stream 4) are fed serially to a hydrogen chloride absorber, caustic scrubber, and drying column to remove hydrogen chloride. The purified methane (Stream 5) is recycled to the chlorination reactor. The condensed crude chloromethane stream (Stream 6) is fed to a stripper, where it is separated into overheads, containing hydrogen chloride, methyl chloride, and some higher boiling chloromethanes, and bottoms, containing methylene chloride, chloroform, and carbon tetrachloride.

Overheads from the stripper (Stream 7) are fed to a water scrubber, where most of the hydrogen chloride is removed as weak hydrochloric acid (Stream 8). The offgas from the water scrubber is fed to a dilute sodium hydroxide scrubber solution to remove residual hydrogen chloride. Water is then removed from the crude chloromethanes in a drying column.

The chloromethane mixture from the drying column (Stream 9) is compressed, condensed, and fed to a methyl chloride distillation column. Methyl chloride from the distillation column can be recycled back to the chlorination reactor (Stream 10) to enhance yield of the other chloromethanes, or condensed and then transferred to storage and loading as product (Stream 11).

Bottoms from the stripper (Stream 12) are neutralized, dried, and combined with bottoms from the methyl chloride distillation column (Stream 13) in a crude storage tank. The crude chloromethanes (Stream 14) pass to three distillation columns in series which extract methylene chloride (Stream 15), chloroform (Stream 17), and carbon tetrachloride (Stream 19). Condensed methylene chloride, chloroform, and carbon tetrachloride product streams are fed to day storage tanks, where inhibitors may be added for stabilization. The product streams are then transferred to storage and loading facilities. Bottoms from the carbon tetrachloride distillation column are typically incinerated.

CHLOROFORM EMISSIONS AND CONTROLS

Documented potential sources of chloroform emissions from chloroform manufacture by the methyl chloride chlorination process include the venting of inert gases from the condenser following the chloroform column, in-process and product storage, loading product chloroform, and process fugitive emission sources such as leaks in process valves, pumps, compressors and pressure relief valves. In the methane chlorination process, chloroform emissions may originate from venting inert gases from the recycle methane stream, the emergency venting of inert gases from the distillation area, in-process and product storage, loading product chloroform, handling and disposal of process waste liquid, and process fugitive sources.[6]

Uncontrolled Emission Factors

Tables 5-2 and 5-3 present uncontrolled emission factors for each of the cited emission sources, from a recent EPA study.[6] These tables include source designations which refer to specific process locations in Figures 5-2 and 5-3. These emission factors are for hypothetical model plants, and actual emissions will vary due to differences in process design, age of equipment and other factors. In the current analysis, these emission factors were used only where recently obtained plant-specific data were not available. Where throughputs for specific types of loading operations were available, the following emission chloroform-specific factors based on the AP-42 loading loss equation were used:

Truck/rail loading with submerged fill: 0.0054 lb/gallon
Barge loading: 0.0045 lb/gallon
Ship loading: 0.0018 lb/gallon

Current Emissions and Controls

Table 5-4 and Figure 5-4 summarize estimated current chloroform emissions from operating chloroform production facilities. Fugitive emissions include process fugitive, loading, and where applicable, secondary emissions from process waste streams. Tables 5-5 through 5-10 provide derivations and sources of the data summarized in Table 5-4, as well as available control information and vent parameters.

Available Control Techniques

Current emission estimates for chloroform production facilities were assessed to determine applicability of available emission control techniques to significant emission sources. Table 5-11 summarizes available control techniques (ACT) resulting from this assessment. These controls apply to storage, handling, and process fugitive emissions at most chloroform plants, and to process emissions at the Diamond Shamrock and Linden Chemicals plants. These control techniques and estimated efficiencies were based on EPA and industry information on existing and feasible controls.

TABLE 5-2. CONTROLLED AND UNCONTROLLED CHLOROFORM EMISSION FACTORS FOR A HYPOTHETICAL CHLOROFORM PRODUCTION FACILITY (METHANOL HYDROCHLORINATION/METHYL CHLORIDE CHLORINATION PROCESS)[a]

Emission source	Source designation[b]	Uncontrolled chloroform emission factor[c]	Available control technique (ACT)	Percent reduction[d]	Controlled chloroform emission factor[e]
Chloroform distillation vent	A	0.022 kg/Mg	None	--	--
Storage					
Crude tank	B	0.061 kg/Mg	Refrigerated condenser	95	0.079 kg/Mg
Surge tank	C	0.097 kg/Mg			
Day tanks (2)	D	0.55 kg/Mg			
Product tank	E	0.87 kg/Mg			
Handling[f]	F	0.35 kg/Mg	Refrigerated condenser	90	0.035 kg/Mg
Process fugitive[g]		1.4 kg/hr	Monthly I/M of valves; double mechanical seals on pumps; rupture disks on relief valves[h]	77	0.32 kg/hr

[a] Any given chloroform production plant may vary in configuration and level of control from this hypothetical facility.

[b] Letters refer to vents designated in Figure 5-2.

[c] Emission factors in terms of kg/Mg refer to kilogram of chloroform emitted per megagram of chloroform produced. In cases where a particular source designation applies to multiple operations, these factors represent combined emissions for all, not each, of these operations within the hypothetical facility. Emission factor derivations are presented in Reference 5.

[d] For refrigerated condensers, ACT removal efficiency is based on a condenser operating temperature of -35°C and an average uncontrolled emission temperature of 20°C for storage and handling. For fugitive emissions, the emission reduction associated with the ACT control alternative is from Reference 5.

[e] Based on uncontrolled emission factor and ACT emission reduction.

[f] Loading of trucks, tank cars, barges.

[g] Fugitive emission rate is independent of plant capacity.

[h] I/M refers to inspection and maintenance.

TABLE 5-3. CONTROLLED AND UNCONTROLLED CHLOROFORM EMISSION FACTORS FOR A HYPOTHETICAL CHLOROFORM PRODUCTION FACILITY (METHANE CHLORINATION PROCESS)[a]

Emission source	Source designation[b]	Uncontrolled chloroform emission factor[c]	Available control technique (ACT)	Percent reduction[d]	Controlled chloroform emission factor[e]
Recycled methane inert gas purge vent	A	0.013 kg/Mg	None	--	--
Distillation area emergency inert gas vent	C	0.032 kg/Mg	None	--	--
Storage					
Crude tank	B	0.088 kg/Mg	Refrigerated condenser	95	0.073 kg/Mg
Day tanks (2)	D	0.55 kg/Mg			
Product tank	E	0.83 kg/Mg			
Secondary	F	0.21 kg/Mg	None	--	--
Handling[f]	G	0.35 kg/Mg	Refrigerated condenser	90	0.035 kg/Mg
Process fugitive[g]		3.1 kg/hr	Monthly I/M of valves; double mechanical seals on pumps; rupture disks on relief valves[h]	76	0.74 kg/hr

[a] Any given chloroform production plant may vary in configuration and level of control from this hypothetical facility.

[b] Letters refer to vents designated in Figure 5-3.

[c] Emission factors in terms of kg/Mg refer to kilogram of chloroform emitted per megagram of chloroform produced. In cases where a particular source designation applies to multiple operations, these factors represent combined emissions for all, not each, of these operations within the hypothetical facility. Emission factor derivations are presented in Reference 5.

[d] For refrigerated condensers, removal efficiency is based on a condenser operating temperature of -35°C and an average uncontrolled emission temperature of 20°C for storage and handling. For fugitive emissions, the emission reduction associated with the ACT control alternative is from Reference 5.

[e] Based on uncontrolled emission factors and ACT emission reduction.

[f] Loading of trucks, tank cars, barges.

[g] Fugitive emission rate is independent of plant capacity.

[h] I/M refers to inspection and maintenance.

TABLE 5-4. CURRENT CHLOROFORM EMISSIONS FROM CHLOROFORM PRODUCTION FACILITIES

		Chloroform emissions (kg/yr)			
Plant	Location	Process	Storage	Fugitive	Total
Diamond Shamrock	Belle, WV	35,800[a]	15,200	38,300	89,300
Dow	Freeport, TX	20	2,920	113,120	116,060
Dow	Plaquemine, TX	9,400[a]	8,600	15,300	33,300
Linden	Moundsville, WV	4,950	21,600	30,440	56,990
Stauffer	Louisville, KY	------------On standby-----------------			
Vulcan	Geismar, LA	310	16,060	26,100	42,470
Vulcan	Wichita, KS	110	72,560	47,000	119,670
TOTAL		50,590	136,940	270,260	457,790

[a] Includes in-process storage.

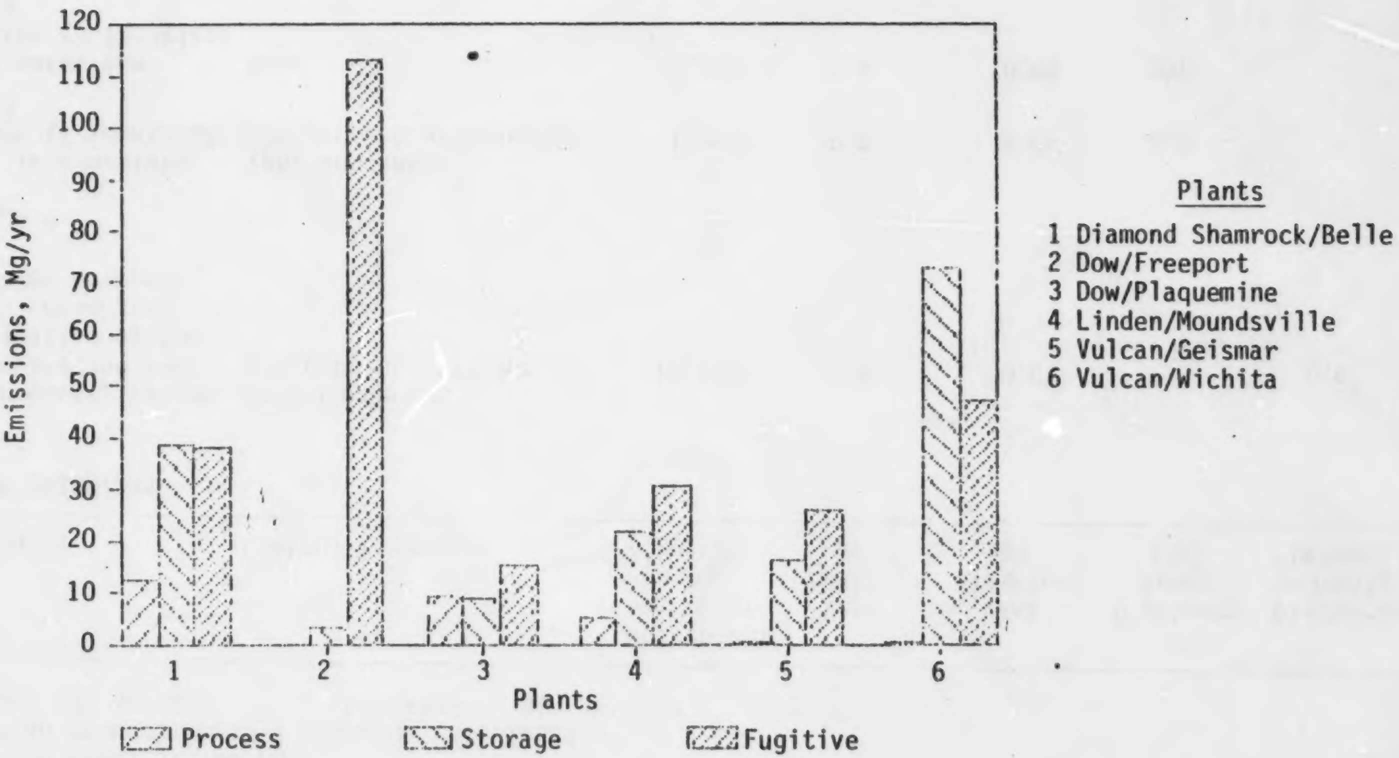


Figure 5-4. Summary of estimated current emissions of chloroform from chloroform production facilities.

TABLE 5-5. EMISSION SUMMARY FOR DIAMOND SHAMROCK/BELLE, WV

Company: Diamond Shamrock
Location: Belle, WV
Production Rate: 12,700 Mg/yr
Production Process: Methyl chloride chlorination
Latitude: 38° 14' 09" Longitude: 81° 32' 38"

Source	Control technique	Chloroform emission rate (kg/yr)	Vent height (m)	Vent diameter (m)	Discharge temp. (°K)	Discharge velocity (m/sec)
CURRENT EMISSIONS						
Process[a]						
Vent recovery system for separation and purification system column condensers and three bottoms tanks	Vent condenser[b] (14 percent efficiency)	12,500	2.4	0.05	296	0.6[c]
Storage[a,d]						
Crude intermediate product (2 identical tanks)	Vent condenser[b] (38 percent efficiency)	1,300	9.7	0.05	302	--
Crude methylene chloride (2 identical tanks)	None	1,760	5.9	0.05	307	--
Crude chloroform tank	None	5,300	4.8	0.05	316	--
In-process chloroform tanks (pre-drier and pre-mole sieve)	None	23,300 	7.9	0.05 0.05	316 327	-- --
Chloroform product day tanks (2 identical tanks)	None	2,160	5.9	0.05	297	--

(CONTINUED)

TABLE 5-5. (continued)

Source	Control technique	Chloroform emission rate (kg/yr)	Vent height (m)	Vent diameter (m)	Discharge temp. (°K)	Discharge velocity (m/sec)
Main chloroform product (3 tanks) and barge loading	Refrigerated vent condenser (92 percent efficiency)	4,320	3.6	0.08	250	--
Mole sieve drain tank, crude product filter feed and organics recovery tanks[e]	None	360	3.0	0.06	297	--
Process fugitive[f]	None assumed	12,300		Area = 40m x 80m		
Handling (truck and rail loading only)[d]	None	830	3.6	0.46	293	--
Secondary[a]						
Mole sieve regeneration vent scrubber[g]	Water scrubber (efficiency unknown)	24,400	7.6	0.25	273-438	--
Scrubber change building	None	770	7.6	0.05	293	--
AVAILABLE CONTROL TECHNIQUE EMISSIONS						
Process						
Vent recovery system for condenser vents from separation and purification system, three bottoms tanks and two in-process chloroform storage tanks[h]	ACT	1,790	15	0.025	230	--

(CONTINUED)

TABLE 5-5. (continued)

Source	Control technique	Chloroform emission rate (kg/yr)	Vent height (m)	Vent diameter (m)	Discharge temp. (°K)	Discharge velocity (m/sec)
Storage						
Crude intermediate product (2 identical tanks)[i]	Existing vent condenser (38 percent efficiency)	1,300	9.7	0.05	302	--
Mole sieve drain tank crude product filter feed and organics recovery tanks[i]	None	360	3.0	0.06	297	--
Main chloroform product (3 tanks) and barge loading[i]	Existing refrigerated vent (92 percent efficiency)	4,320	3.6	0.08	250	--
Crude methylene chloride and chloroform tanks (2 each); chloroform day tanks (2)	ACT	460	15	0.025	238	--
Process fugitive	ACT	2,800		Area = 40m x 80m		
Handling	ACT	80	15	0.025	238	
Secondary						
Mole sieve regeneration vent scrubber[j]	Water scrubber (efficiency unknown)	24,400	7.6	0.25	273-438	
Scrubber change building[k]	None	770	7.6	0.05	293	

(CONTINUED)

TABLE 5-5. (continued)

Source	Control technique	Chloroform emission rate (kg/yr)	Vent height (m)	Vent diameter (m)	Discharge temp. (°K)	Discharge velocity (m/sec)

[a] Emission rates, controls and vent parameters from Reference 7, except where noted.

[b] River water condensers.

[c] Reference 8.

[d] Emissions have been combined for tanks with the same vent parameters and controls.

[e] Vent parameters averaged for these minor sources.

[f] Based on emission factor (Table 5-2) and 8760 hour/year operation.

[g] An intermittent source with large air flow and variable temperatures and chloroform concentrations during the regeneration cycle.

[h] Based on available ACT, combining two in-process storage tanks and current process emissions (see text).

[i] ACT not applied due to distance from other storage sources, low emissions and/or current control.

[j] No ACT due to intermittent, variable nature of source.

[k] No ACT due to low emissions.

TABLE 5-6. EMISSION SUMMARY FOR DOW/FREEPORT, TX

Company: Dow
Location: Freeport, TX
Production Rate: 35,700 Mg/yr
Production Process: Methyl chloride chlorination
Latitude: 28° 59' 30" Longitude: 95° 23' 35"

Source	Control technique	Chloroform emission rate (kg/yr)	Vent height (m)	Vent diameter (m)	Discharge temp. (°K)	Discharge velocity (m/sec)
CURRENT EMISSIONS						
Process[a]						
Chloroform distillation vent	Thermal oxidation (99.9+ percent efficiency)	20	13.0	0.51	294	0.027
Storage[a]						
Product	Refrigerated condenser (88 percent efficiency)	1,690	15.2	0.102	253	--
Product	None	1,230	6.1	0.051	294	--
Process fugitive[b]	None	94,000	Area = 40m x 80m			
Handling[c]						
Truck/rail	None	5,850				
Drums[d]	None	1,170				
Barge	None	7,780				
Ship	None	4,320				
AVAILABLE CONTROL TECHNIQUE EMISSIONS						
Process						
Chloroform distillation vent	None	20	13.0	0.51	294	0.027

(CONTINUED)

TABLE 5-6 (continued)

Source	Control technique	Chloroform emission rate (kg/yr)	Vent height (m)	Vent diameter (m)	Discharge temp. (°K)	Discharge velocity (m/sec)
Storage						
Product (combined)	ACT	770	15	0.025	238	--
Process fugitives	ACT	21,600		Area = 40m x 80m		
Handling[e]						
Truck and rail	ACT	580	15	0.025	238	--
Barge and ship	ACT	1,210	15	0.025	238	--
Drums	None	1,170		Area = 40m x 80m		

[a] Emission rates, controls and vent parameters from Reference 9.

[b] Based on reported fugitive emission sources in Reference 9 and emission factors from Reference 22.

[c] Based on annual loading throughputs from Reference [illegible] and emission factors cited in text.

[d] Truck/rail emission factor used for drum loading.

[e] Truck and rail loading assumed vented to one control system, barge and ship to another. No control assumed for drum loading.

TABLE 5-7. EMISSION SUMMARY FOR DOW/PLAQUEMINE, LA

Company: Dow
Location: Plaquemine, LA
Production Rate: 35,700 Mg/yr
Production Process: Methyl chloride chlorination
Latitude: 30° 19' 00" Longitude: 91° 15' 00"

Source	Control technique	Chloroform emission rate (kg/yr)	Vent height (m)	Vent diameter (m)	Discharge temp. (°K)	Discharge velocity (m/sec)
CURRENT EMISSIONS						
In-process storage and chloroform distillation column[a]	None	9,400	12	0.46	303	2.7
Storage[a]	Refrigerated condensers (90 percent efficiency)	8,600	15	0.025	253	--
Process fugitive[b]	I/M of valves; mechanical seals on pump and compressors (77 percent efficiency)[c]	2,800		Area = 40m x 80m		
Handling[b] (tank cars only[a])	None	12,500				
AVAILABLE CONTROL TECHNIQUE EMISSIONS						
In-process storage and chloroform distillation column	None	9,400	12	0.46	303	2.7
Storage	Existing	8,600	15	0.025	253	--
Process fugitive	Existing	2,800				
Handling	ACT	1,250	15	0.025	238	

(CONTINUED)

TABLE 5-7. (continued)

Source	Control technique	Chloroform emission rate (kg/yr)	Vent height (m)	Vent diameter (m)	Discharge temp. (°K)	Discharg velocity (m/sec)

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[a] Emission rates and controls from Reference 10, vent parameters from Reference 11.

[b] Based on emission factors (Table 5-2). Fugitive control efficiency from Table 5-2, based on information in Reference 10.

TABLE 5-8. EMISSION SUMMARY FOR LINDEN/MOUNDSVILLE, WV

Company: Linden
Location: Moundsville, WV
Production Rate: 14,300 Mg/yr
Production Process: Methyl chloride chlorination
Latitude: 39° 54' 20" Longitude: 80° 48' 10"

Source	Control technique	Chloroform emission rate (kg/yr)	Vent height (m)	Vent diameter (m)	Discharge temp. (°K)	Discharge velocity (m/sec)
CURRENT EMISSIONS[a]						
Chloroform distillation vent condenser	Well water condenser (82 percent control)	4,950	10.4	0.05	291	0.49
Storage						
Recovery tank	None	1,000	2.8	0.05	308	--
Methylene bottoms tank	None	4,800	3.7	0.05	298	--
Chloroform storage	None	15,800	7.6	0.1	293	--
Process fugitives[b]	None	17,700	Area = 40m x 80m			
Handling						
Rail	None	11,900				
Secondary						
Spent caustic	None	730				
Spent sulfuric acid	None	110				
AVAILABLE CONTROL TECHNIQUE EMISSIONS						
Chloroform distillation vent condenser	ACT	250	15	0.025	230	
Storage						
Recovery tank	None	1,000	2.8	0.05	308	
Methylene bottoms tank	None	4,800	3.7	0.05	298	--

(CONTINUED)

TABLE 5-8. (continued)

Source	Control technique	Chloroform emission rate (kg/yr)	Vent height (m)	Vent diameter (m)	Discharge temp. (°K)	Discharge velocity (m/sec)
Chloroform storage	ACT	790	15	0.025	238	--
Process fugitives	ACT	4,070		Area = 40m x 80m		
Handling	ACT	1,190	15	0.025	238	--
Secondary	None	840		Area = 40m x 80m		

[a] Emissions, controls and vent parameters from Reference 12, except where noted.

[b] Based on reported fugitive emission sources in Reference 12 and emission factors in Reference 22.

TABLE 5-9. EMISSION SUMMARY FOR VULCAN/GEISMAR, LA

Company: Vulcan
Location: Geismar, LA
Production Rate: 21,400 Mg/yr
Production Process: Methyl chloride chlorination
Latitude: 30° 10' 00" Longitude: 90° 59' 00"

Source	Control technique	Chloroform emission rate (kg/yr)	Vent height (m)	Vent diameter (m)	Discharge temp. (°K)	Discharge velocity (m/sec)
CURRENT EMISSIONS[a]						
Chloroform tower	None	310	9.1	0.24	316	--
Storage						
Check tanks (2)	None	1,560	3.1	0.20	293	--
Check tanks (2)	None	3,600	3.7	0.05	293	--
Chloroform storage (2)	Vapor recovery(90 percent efficiency)	5,600	0	0.10	293	--
Chloroform storage	Vapor recovery(90 percent control)	5,300	0	0.15	293	--
Process fugitive[b]	None	12,300	Area = 40m x 80m			
Handling[c]						
Tank car rack	Thermal oxidation (99.9+ percent control when on line)	4,700				
Tank truck racks (2)		2,400				
Secondary						
Molecular sieve bed vent[d]	None	4,500	9.2	0.15	533	2.0
Waste neutralizer tank[e]	None	2,200	6.1	4.3	293	--

(CONTINUED)

TABLE 5-9. (continued)

Source	Control technique	Chloroform emission rate (kg/yr)	Vent height (m)	Vent diameter (m)	Discharge temp. (°K)	Discharge velocity (m/sec)
AVAILABLE CONTROL TECHNIQUE EMISSIONS						
Chloroform tower	None	310	9.1	0.24	316	--
Storage						
Check tanks (2)	None	1,560	3.1	0.20	293	--
Check tanks (2)	None	3,600	3.7	0.05	293	--
Chloroform storage (2)	Existing	5,600	0	0.10	293	--
Chloroform storage	Existing	5,300	0	0.15	293	--
Process fugitive	ACT	2,800		Area = 40m x 80m		
Handling						
Tank car rack	Existing	4,700				
Tank truck racks (2)		2,400				
Secondary						
Molecular sieve bed vent	None	4,500	9.2	0.15	533	2.0
Waste neutralizer tank	None	2,200	6.1	4.3	293	--

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[a] From Reference 13 unless otherwise noted.

[b] Based on emission factor, Table 5-2.

[c] These handling emissions are totals for drying of tanks and for uncontrolled periods when the main incinerator is off line. Post-incinerator emissions are assumed to be negligible in Reference 13.

[d] Assumed to be intermittent emissions from molecular sieve regernation.

[e] Apparently an open tank for neutralization of a variety of waste streams. All reported chloroform emissions assumed to be due to chloroform production.

TABLE 5-10. EMISSION SUMMARY FOR VULCAN/WICHITA, KS

Company: Vulcan
Location: Wichita, KS
Production Rate: 26,600 Mg/yr by methyl chlorination; 13,100 Mg/yr by methane chlorination
Production Process: 67% methyl chloride chlorination; 33% methane chlorination[a]
Latitude: 37° 36' 55" Longitude: 97° 18' 30"

Source	Control technique	Chloroform emission rate (kg/yr)	Vent height (m)	Vent diameter (m)	Discharge temp. (°K)	Discharge velocity (m/sec)
CURRENT EMISSIONS[a]						
Reflux drum	*	110				
Storage						
Nine uncontrolled tanks*	None	2,700				
		2,700				
		2,700				
		3,530				
		20,550				
		16,420				
		180				
		20,550				
		2,410				
Two controlled tanks*	*(89 percent control)	410				
		410				
Fugitive process[b]	None assumed	40,200				
Handling	None assumed	6,800				

*NOTE: Source description, vent parameters and control data are in CPB Confidential file.

(CONTINUED)

TABLE 5-10 (continued)

Source	Control technique	Chloroform emission rate (kg/yr)	Vent height (m)	Vent diameter (m)	Discharge temp. (°K)	Discharge velocity (m/sec)
AVAILABLE CONTROL TECHNIQUE EMISSIONS						
Reflux drum	*	110				
Storage	ACT for all tanks	3,950	15	0.025	238	--
Fugitive process	ACT	9,250		Area = 90m x 100m		
Handling	ACT	680	15	0.025	238	--

[a] From Reference 14, except where noted.

[b] Based on reported fugitive emission sources in Reference 14 and emission factors from Reference 22.

TABLE 5-11. AVAILABLE CONTROL TECHNIQUES FOR CHLOROFORM PRODUCTION FACILITIES

Source category	Control technique	Estimated efficiency (%)
Column vents[a]	Refrigerated condensation	95[b]
Storage	Vapor recovery and -35°C refrigerated condensation	95[b]
Process fugitives	Monthly leak detection and repair; equipment specifications	77[c]
Handling	Vapor recovery, -35°C refrigerated condensation and leakage reduction	90[b]

[a] Diamond Shamrock, Belle, WV, and Linden, Moundsville, WV.

[b] See text for control efficiency derivations.

[c] For methyl chloride chlorination. Methane chlorination process efficiency is 76 percent. From Tables 5-2 and 5-3.

Process vent emissions are reported to be less than one percent of current total plant emissions for three of the chloroform production processes. A pressure-relief valve venting the chloroform distillation column and in-process storage at Dow/Plaquemine, LA accounts for 23 percent of the current plant total, or about 8 percent of total uncontrolled emissions. The intermittent nature of this source is not amenable to available standard control devices for volatile organics, although some process modifications may be feasible. Thus, controls were not specified for process emissions at these four plants.

Due to the large total process emissions reported for the Diamond Shamrock methyl chloride chlorination process at Belle, WV, available emission data were used to design a refrigerated condenser which would provide control of combined process emissions. Choice of a small refrigerated condenser was based on current use of river water condensers on these process streams. Other options include carbon adsorption, solvent absorption, and thermal oxidation. Carbon adsorbers and solvent absorption are considerably more complex than a condenser, and would be hard to justify in a retrofit situation. Thermal oxidation would require auxiliary fuel, because the principal components of this vent stream (methylene chloride and chloroform) are nonflammable. It also would not result in recovery of product. Based on the theoretical correlation between vapor pressure reduction and emission control for a properly-sized condenser, a -43°C condenser would provide an additional 95 percent control of the existing 7°C process streams at this plant. This control requirement was based on the best available data on characteristics of the process emissions.[7,15,16] The available data on process emissions at Linden Chemical in Moundsville, WV, indicate that a similar condenser could provide similar control at that plant.

Similar condenser efficiency estimates were the basis for potential storage and handling controls. A 95 percent control level for chloroform storage requires a condenser at -35°C, based on a 20°C ambient temperature and assuming proper sizing and design to achieve maximum effectiveness.

Refrigerated condensation was chosen mainly because it is the principal control currently in use for halogenated chemical storage. Refrigerated condensation is used at six of the seven currently controlled chloroform storage facilities cited in this chapter and Chapter 6. One fluorocarbon 22 plant (Allied/El Segundo, CA) uses pressurized storage. Although the size of this tank is not known, available production and emission data indicate that it is the smallest fluorocarbon 22 plant, and that the tank is quite small relative to those at other plants. Since pressurized storage is only a practical control alternative for small fixed-roof tanks, it is not applicable to the larger tanks at chloroform production plants. Refrigerated condensation can be applied to existing fixed roof chloroform storage tanks without taking them out of operation, a factor which may be critical for installation of controls at the three chloroform plants which have only one main chloroform product storage tank.

Other options for control of emissions from storage of volatile organic compounds include: (1) rim-mounted secondary seals or fixed-roofs on external floating roof tanks, (2) internal floating roofs on fixed roof tanks, (3) rim-mounted secondary seals or contact internal floating roofs for noncontact internal floating roof tanks, (4) liquid-mounted primary seals on contact internal floating roofs, (5) rim-mounted secondary seals on contact internal floating roofs, (6) carbon adsorption, (7) thermal oxidation, and (8) pressure vessels. Option 1 does not apply in this case because external floating roofs are not used for organic chemical storage (they are generally used only on large tanks for petroleum liquids). Options 2, 3, 4, and 5 involve various configurations of internal floating roofs. Although floating roofs can provide control comparable to refrigerated condensers, chloroform's ability to dissolve rubber floating roof components would be a problem for typical floating roofs. Use of special materials may overcome this problem, but lack of industry experience and information on potential rubber substitutes prevent further consideration of these options. The need to empty and clean tanks for floating roof installation could also be a constraint at plants without available alternate storage.

Carbon adsorbers (Option 6) are not known to be used for control of emissions from storage of organic chemicals, although they can provide comparable control. Adsorbers are likely to require significantly more operating labor or more sophisticated instrumentation to ensure efficient desorption cycles under fluctuating input conditions. Provision of cooling water and steam or vacuum for regeneration may be a consideration in the vicinity of existing tanks. Disposal of cooling water, condensate and spent carbon are additional considerations which are not encountered with condensers. Thermal oxidation (Option 7) is not a preferred option for chloroform emissions alone, because chloroform is nonflammable and would require auxiliary fuel or joint control of more combustible hydrocarbons for effective control. In addition, no chloroform recovery is possible with thermal oxidation. As stated above, pressure vessels (Option 8) are not practical for the size of main storage tanks used at chloroform plants. Use of pressure vessels would also require abandoning existing fixed-roof tanks and building new pressure vessels, which would be very expensive relative to the add-on control options discussed above.

For control of handling emissions, the principal options are refrigerated condensers, carbon adsorbers, and thermal oxidation. As discussed for storage controls, carbon adsorbers and thermal oxidation have significant disadvantages relative to refrigerated condensers, so a vapor recovery system with a -35°C refrigerated condenser was chosen as ACT. In this case, the theoretical condenser efficiency of 95 percent was reduced to a practical level of 90 percent due to incomplete capture of vapor recovery systems.[17]

The fugitive control technique cited in Table 5-11 is based on monthly inspection and repair of valves and pumps in light liquid and gas service, and equipment specifications including rupture disks on gas safety/relief valves, plugs and caps on open-ended lines, closed purge systems on sampling connections and vented seal areas on compressors (flanges are not controlled). This combination is estimated to have an overall fugitive emission control efficiency of 76 to 77 percent for typical chloroform production facilities,[6] and was chosen because it was selected as best demonstrated technology (BDT) for the new source performance standard (NSPS) for synthetic organic chemical manufacturing fugitive emissions.

A number of secondary emission points have been reported for chloroform production, including regeneration of molecular sieves at two plants, a waste neutralization tank and handling of spent caustic and sulfuric acid. No ACT were developed for these emissions, due to the intermittent, highly variable nature of molecular sieves regeneration and the minor contribution of the other reported emissions.

Tables 5-5 through 5-10 include the application of ACT control efficiencies to available current emission estimates, to estimate feasible emission control levels. Existing storage controls with efficiencies of 90-percent or greater were assumed to remain in place under ACT. In cases where available descriptions of plant layout made it possible to identify in-process storage or other tanks which would not be co-located with the main storage tanks, these tanks were not controlled at the ACT level. Where data on tank types were not available, ACT was applied to all storage emissions, which probably overestimates the potential control. Vent parameters for ACT were based on model plant parameters[4,5] and assumed condenser exit temperatures. Table 5-12 summarizes ACT emissions.

CONTROL COSTS

The following estimates of costs of available control techniques (ACT) for chloroform production facilities are based on previous EPA studies of applicable control programs and technologies, with additional data on capital costs and utility usage supplied by industrial vendors. All costs are for July 1982.

Process Control Costs

As stated in the preceding section, the only ACT for process emissions are refrigerated condensers which would be retrofitted to existing river water condensers on process vents at Diamond Shamrock/Belle, WV and Linden/Moundsville, WV. Based on available technical data for Diamond Shamrock process emissions,[15,16] a tentative condenser design for 95 percent control of chloroform was performed. This condenser would run at about -40°C, handle a flow of 4.4 acfm and requires cooling capacity of about 9,000 BTU/hr. Along with 95 percent control of a current chloroform emission rate of 7.5 kg/hr, this condenser would also control other process vent components at about the same efficiency. These components include 21.2 kg/hr of methylene chloride and 0.5 kg/hr of carbon

TABLE 5-12. CHLOROFORM EMISSIONS FROM CHLOROFORM PRODUCTION FACILITIES WITH AVAILABLE CONTROL TECHNIQUES

Plant	Location	Chloroform emissions (kg/yr) Process	Storage	Fugitive	Total
Diamond Shamrock	Belle, WV	1,790[a]	6,440	28,050	36,280
Dow	Freeport, TX	20	770	24,560	25,350
Dow	Plaquemine, TX	9,400[a]	8,600	4,050	22,050
Linden	Moundsville, WV	250	6,590	6,100	12,940
Stauffer	Louisville, KY	----------------On standby----------------			
Vulcan	Geismar, LA	310	16,060	16,600	32,970
Vulcan	Wichita, KS	110	3,950	9,930	13,990
TOTAL		11,880	42,410	89,290	143,580

[a] Includes in-process storage.

tetrachloride. The following cost estimate considers only recovery of chloroform, since it is the pollutant of concern in this analysis. Credit for recovery of other components would improve the cost effectiveness of this condenser.

Condensers with the low temperature and small cooling requirement cited above are not standard units in a major manufacturer's line. With engineering costs, a customized unit could probably be built for $15,000.[18] Additional allowances of 18 percent of base cost for taxes, freight and instrumentation and 74 percent for installation[19] result in an installed capital cost of $30,800. A previous analysis for refrigerated condensers estimated an overall annualized capital cost factor of 29 percent, which includes maintenance labor and material (6 percent), taxes, insurance and administration (5 percent) and a capital recovery factor (18 percent).[20] Applying this factor results in an annualized capital cost of about $8,900. Based on electric utility usage rates provided by a manufacturer, this unit would use about 5 kW/hr. Full-time operation at a cost of $0.08/kWh[21] would result in an annual utility bill of $3,500. Assuming an operating labor requirement of about $19/hour,[20] an annual labor cost of about $3,500 was estimated. With the emission reduction cited in Table 5-5 and 5-8, the following estimates of net cost and cost-effectiveness were made.

Base capital cost	$ 15,000
Installed capital cost	30,800
Annualized capital cost	8,900
Utilities	3,500
Operating labor	3,500
Annual cost	$ 15,900

	Diamond Shamrock	Linden
Recovery credit	($23,200)	($3,200)
Net annual cost (credit)	($7,300)	$12,700
Emission reduction	34.0 Mg/yr	4.7 Mg/yr
Cost-effectiveness (credit)	($214/Mg)	$ 2,700/Mg

Process Fugitive Control Costs

Available control technique for process fugitive emissions is a program combining monthly inspection and repair of potential emission sources with equipment specifications for safety/relief valves, compressor seals and sampling connections. The control costs estimated below are based on two different model plant sizes from a recent EPA study of fugitive emission control costs in the synthetic organic chemical manufacturing industry (SOCMI).[22] As shown in Table 5-13, the numbers of fugitive emission sources in these SOCMI model plants are somewhat greater than the numbers estimated to be in chloroform service in the model plants for methyl chloride chlorination and methane chlorination, and it is known that the number of fugitive sources varies substantially from the model plants in several cases. For the purposes of this study, however, it was assumed that the SOCMI model plant costs could be used directly. Table 5-14 presents the results of applying the annualized costs below to estimated emission reduction for the plants applying ACT in Table 5-5 through 5-10. The methyl chloride chlorination model plant costs apply to the production facilities using the process for which ACT is specified in Tables 5-5 through 5-10 (Diamond Shamrock/Belle WV, Dow/Freeport TX, Linden/Moundsville, WV and Vulcan/Geismar, LA). Since both processes exist at Vulcan/Wichita KS, the two sets of costs would be combined for a total facility control cost there.

	Methyl chloride chlorination model plant	Methane chlorination model plant
Total installed capital cost	$30,700	$77,600
Total annualized cost	$18,800	$50,700

TABLE 5-13. MODEL PLANT FUGITIVE EMISSION SOURCES

	Methyl chloride chlorination model plant		
	Total fugitive sources[5]	In chloroform service[23]	Small SOCMI fugitives model plant[22]
Pumps	30	6	8
Process valves	725	184	230
Relief valves	25	6	13
Compressors	2	0	1
	Methane chlorination model plant		
	Total fugitive sources[6]	In chloroform service[23]	Medium SOCMI fugitives model plant[22]
Pumps	80	15	29
Process valves	1,930	596	926
Relief valves	70	15	50
Compressors	1	0	2

TABLE 5-14. CONTROL COSTS FOR PROCESS FUGITIVES AT CHLOROFORM PRODUCTION FACILITIES (July 1982 $)

	Diamond Shamrock Belle, WV	Dow Freeport, TX	Linden Moundsville, WV	Vulcan Geismar, LA	Vulcan Wichita, KS
Annual cost	18,800	18,800	18,800	18,800	69,500
Recovery credit[a]	(6,500)	(49,400)	(9,300)	(6,500)	(21,100)
Net annual cost[a]	12,300	(30,600)	9,500	12,300	48,400
Emission reduction (Mg/yr)	9.5	72.4	13.6	9.5	31.0
Cost effectiveness ($/Mg)[a]	1,290	(420)	700	1,290	1,560

[a] ( ) indicates a credit due to chloroform recovery, based on emission reductions for process fugitive ACT from Tables 5-5 through 5-10.

Storage Control Costs

The controlling factor in size and cost of the ACT refrigerated condenser for chloroform storage is the displacement of vapors caused by transfer from day tanks to bulk storage. A 200 gallon/minute pumping rate was reported for the Vulcan facility at Geismar, LA.[24] Base capital cost for a condenser to handle this displacement would be about $45,000.[18] It is assumed that this operating rate and capital costs would apply to storage at all four chloroform facilities to which ACT applies. The factors for installed cost and annualized capital cost discussed under Process Control Costs also apply here, resulting in the costs shown in Table 5-15. Utility and labor costs were also estimated using the same basic assumptions and rates described for process controls. The basis for the costs in Table 5-15 is an operating time of about 300 hours, based on the annual transfer time which would be required for the estimated annual production at Vulcan/Geismar. Expected emission reductions from Tables 5-5 through 5-10 were used to estimate recovery credits, net annual cost and cost-effectiveness of control at each facility.

Handling Control Costs

Estimating costs for ACT control of handling emissions (vapor recovery systems with refrigerated condensers) is subject to considerable uncertainty due to lack of data on the characteristics of existing tank trucks, tank cars, ships and barges, chemical loading facilities and on the cost of vapor recovery systems for them. A cost of about $2,000 for retrofitting gasoline tank trucks for vapor recovery has been estimated.[25] Without adequate supporting data, it is impossible to include these items in this analysis, and the costs below are based on available condenser costs and available data on loading operations. This results in a rough, worst-case estimates of control costs. In particular, potential costs for smaller facilities may be substantially overestimated.

One source reported a single loading rack operation rate of 200 gallons/minute, at a facility with two truck-loading racks and two tank car racks.[24] Assuming no more than two racks loading chloroform at once, a base condenser cost of $100,000 is estimated for tank truck and tank car loading at all facilities where

TABLE 5-15. CONTROL COSTS FOR STORAGE AT CHLOROFORM PRODUCTION FACILITIES (July 1982 $)

	Diamond Shamrock Belle, WV	Dow Freeport, TX	Linden Moundsville, WV	Vulcan Wichita, KS
Base capital cost	$45,000	$45,000	$45,000	$45,000
Installed capital cost	92,400	92,400	92,400	92,400
Annualized capital cost	26,800	26,800	26,800	26,800
Utilities	3,400	3,400	3,400	3,400
Operating labor	600	600	600	600
Annual cost	$30,800	$30,800	$30,800	$30,800
Recovery credit[a]	(6,000)	(1,500)	(10,200)	(46,800)
Net annual cost[a]	$24,800	$29,300	$20,600	($16,000)
Emission reduction (Mg/yr)[a]	8.8	2.2	15.0	68.6
Cost effectiveness ($/Mg)[a]	2,800	13,300	1,370	(230)

---

[a] ( ) indicates a net credit due to chloroform recovery, based on emission reductions between current storage emissions and ACT storage emissions (Tables 5-5 through 5-10).

ACT applies.[18] The same base cost has been used for control of barge and ship loading at Dow/Freeport, assuming that marine loading facilities are not close enough to truck and rail loading racks to allow use of a single condenser. Marine loading rates may be higher than the total 400 gallons/minute assumed for truck and rail racks, but condenser costs are not directly proportional to loading rate, and information is not available for a more specific estimate. Applying the installation and annualization factors discussed under Process Control Costs results in the installed and annualized capital costs shown below. Worst-case utility and labor costs were also estimated using the same basic assumptions and rates described for process controls, based on the hours required in a year for loading of the largest plant's estimated production at 200 gallons per minute. The total loading time estimated for Vulcan/Wichita was about 600 hours per year. It was assumed that vapor recovery and condensation equipment would be operated only during loading, and that labor requirements for operation of the control system would also be equal to the estimated loading time. Electric usage was estimated to 50 kW/hr.

	Control costs for one loading location
Base capital cost	$ 100,000
Installed capital cost	205,000
Annualized capital cost	59,500
Utilities	2,400
Operating labor	11,400
Annual cost	$ 73,300

Emission reductions, recovery credits, and cost-effectiveness were estimated by applying the costs above to the total handling emission reductions for ACT in Tables 5-5 through 5-10, as shown in Table 5-16.

TABLE 5-16. CONTROL COSTS FOR HANDLING AT CHLOROFORM PRODUCTION FACILITIES (July 1982 $)

	Diamond Shamrock Belle, WV	Dow Freeport, TX	Dow Plaquemine, LA	Linden Moundsville, WV	Vulcan Wichita, KS
Annual cost	$73,300	$146,600	$73,300	$73,300	$73,300
Recovery credit[a]	(480)	(11,050)	(7,710)	(7,300)	(4,160)
Net annual cost	72,820	135,600	65,600	66,000	69,140
Emission reduction (Mg/yr)	0.7	16.2	11.3	10.7	6.1
Cost effectiveness ($/Mg)	10,400	8,370	5,800	6,170	11,330

[a] ( ) indicates a credit due to chloroform recovery.

Basis of Control Costs

All costs are in July 1982 dollars. Costs in original references were inflated to July 1982 using the Chemical Engineering plant cost index.[26] When estimation of capital and annual costs was necessary, cost factors cited in available EPA cost data references were used on the assumption that they are more applicable than more generalized cost factors from other sources.

Emission reductions and product recovery credits for estimated best controls were based only on chloroform emissions. Other compounds would also be controlled by process and process fugitive controls, and consideration of recovery credits for them would reduce the net costs of these controls. The July 1982 price for chloroform used in computing recovery credits was $682/Mg ($0.33/lb).[27]

Summary

Table 5-17 presents a summary of estimated costs for implementation of ACT controls at chloroform production facilities.

COST-EFFECTIVENESS

Table 5-18 presents a summary of the estimated cost-effectiveness of the available control techniques discussed above. This summary illustrates the variability of ACT cost-effectiveness across plants and control types. In some cases, relatively higher cost-effectiveness of controls is due to some level of existing control and the correspondingly lower potential emission reduction for ACT. For example, Dow/Freeport, TX currently controls storage emissions at 88 percent efficiency, and ACT is credited only with the marginal control to 95 percent. In other cases, the scale of given plants and control costs based on model plants or other point estimates may result in higher cost-effectiveness for small plants and efficiencies of control for larger plants. For example, the model plant fugitive control cost and relatively high estimated fugitive emissions result in a substantial credit for fugitive control at Dow/Freeport. On the average, however, it appears that control of handling emissions is the most costly per megagram of chloroform controlled, while process vent controls and process fugitive controls are somewhat less expensive than storage controls.

TABLE 5-17. NET ANNUAL CONTROL COSTS FOR AVAILABLE CONTROL TECHNIQUES AT CHLOROFORM PRODUCTION FACILITIES (July 1982 $)

		Process	Process fugitives	Storage	Handling	Total
Diamond Shamrock	Belle, WV	(7,300)[a]	12,300	24,800	72,800	102,620
Dow	Freeport, TX	--[b]	(30,600)	30,000	135,600	135,000
Dow	Plaquemine, LA	--	--	--	65,600	65,600
Linden	Moundsville, WV	12,700	8,600	20,600	66,000	107,900
Stauffer	Louisville, KY	----------On Standby----------				
Vulcan	Geismar, LA	--	12,300	--	--	12,300
Vulcan	Wichita, KS	--	48,400	(16,000)	69,140	101,540
TOTAL		5,400	51,000	59,400	409,160	524,960

[a] ( ) indicates a net credit due to chloroform recovery.

[b] -- indicates no ACT required..

TABLE 5-18. COST-EFFECTIVENESS OF AVAILABLE CONTROL TECHNIQUES AT CHLOROFORM PRODUCTION FACILITIES (July 1982 $/Mg)

		Process	Process fugitives	Storage	Handling	Average
Diamond Shamrock	Belle, WV	(214)[a]	1,290	2,800	10,400	1,940
Dow	Freeport, TX	--[b]	(420)	13,300	8,370	1,490
Dow	Plaquemine, LA	--	--	--	5,800	5,800
Linden	Moundsville, WV	2,700	700	1,370	6,170	2,450
Stauffer	Louisville, KY	----------On Standby----------				
Vulcan	Geismar, LA	--	1,290	--	--	1,290
Vulcan	Wichita, KS	--	1,560	(230)	11,330	960
Average		140	380	630	9,090	1,670

[a] ( ) indicates a net credit due to chloroform recovery.

[b] -- indicates no ACT required.

CONCLUSIONS

This preliminary analysis indicates that current chloroform emissions from the six operating chloroform production facilities can be reduced from about 458 Mg/yr to 144 Mg/yr, through the use of available control techniques This overall 69 percent reduction is due mostly to control of process fugitive emissions and storage emissions, which represent 43 and 30 percent of the total potential control, respectively. Process fugitive controls are reportedly in practice at only one plant, while storage emissions are controlled to at least 90 percent efficiency at two plants. Control of handling emissions accounts for 14 percent of potential overall control with only one plant currently controlling product loading. Control of significant process vent emissions at two plants account for the remaining 12 percent of potential control. As shown in Table 5-12, about 62 percent of the 144 Mg/yr remaining after application of ACT are fugitive emissions, principally the portion of process fugitives not affected by ACT, and uncontrolled secondary emission sources. In-process storage tanks not covered by ACT due to distance from principal product storage are a large part of the remaining process and storage emissions.

The total estimated net national cost for implementation of ACT for all sources in the chloroform production industry would be about $525,000 per year, almost $410,000 or 78 percent of which is for control of handling emissions. Almost all of the remaining net control cost is divided between process fugitive and storage controls ($51,000 and $59,000 respectively). Net costs for individual controls vary widely between plants, depending on controls already in place and credits for recovered chloroform. Total estimated annual costs per plant vary from $12,300 for a plant with many ACT controls in place (Vulcan/Geismar, LA), to $435,000 for a plant assumed to require two handling control systems, for truck/rail and marine loading, as well as controls on process fugitives and storage. Cost-effectiveness of individual ACT controls were estimated to range from a credit of $420/Mg of chloroform controlled to a cost of $13,300/Mg. Combined cost-effectiveness of all ACT controls for specific plants ranged from $960/Mg to $5,800/Mg. Handling control systems were the most expensive on average, at $9,100/Mg, with storage and process fugitives at $630/Mg and $380/Mg, respectively.

Process vent control was estimated at $2,700/Mg and a credit of $214/Mg for the two plants with ACT for process vents.

It should be noted that this analysis is based on the inventory of currently-operating plants, which does not include a Stauffer plant at Louisville, KY, reportedly permanently closed, or the planned construction of a large facility by DuPont in Corpus Christi, TX, by late 1985.

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6. FLUOROCARBON 22 PRODUCTION

INTRODUCTION

The primary use of chloroform is as a feedstock for the production of chlorodifluoromethane, fluorocarbon 22 ($CHClF_2$). Recent estimates of the proportion of total domestic chloroform production used in fluorocarbon 22 production range up to 90 percent. The principal uses of fluorocarbon 22 are as a refrigerant (accounting for 60 to 65 percent of recent chloroform production), and as an intermediate in production of fluoropolymers (using 20 to 30 percent of chloroform production). A small amount of fluorocarbon 22 is also used as an aerosol propellant.[1,2]

There are currently six facilities in the United States that produce fluorocarbon 22 on a routine basis, and one which may operate on a non-routine basis. These plants are listed in Table 6-1; the production locations are shown on Figure 6-1. Published statistics on fluorocarbon 22 production are not available. References indicate that the Allied plants in Elizabeth, NJ and El Segundo, CA, typically produce 12,100 and 2,600 Mg/yr of fluorocarbon 22, and that DuPont production at Louisville, KY is about 45,000 Mg/yr.[4,6] Because data are not available on the non-routine production of fluorocarbon 22 at the DuPont Montague, MI facility, it will not be addressed further in this report.

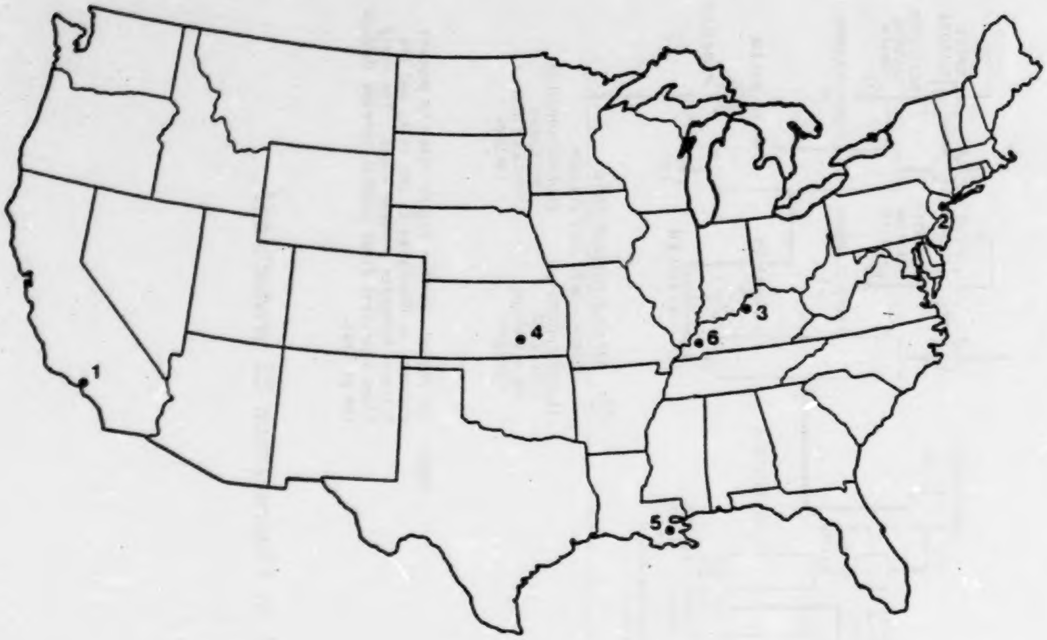
SOURCE DESCRIPTION

Fluorocarbon 22 is produced by the catalytic liquid-phase reaction of anhydrous hydrogen fluoride (HF) and chloroform. Basic operations that may be used in the production of fluorocarbon 22 are shown in Figure 6-2. Chloroform (Stream 1), liquid anhydrous HF (Stream 2), and chlorine (Stream 3) are pumped from storage to the reactor, along with the recycled bottoms from the product recovery column (Stream 15) and the HF recycle stream (Stream 9). The reactor contains antimony pentachloride as a catalyst[7] and is operated at temperatures ranging from 0 to 200°C and pressures of 100 to 3,400 kPa.[8]

TABLE 6-1. FLUOROCARBON 22 PRODUCTION FACILITIES[3,4,5]

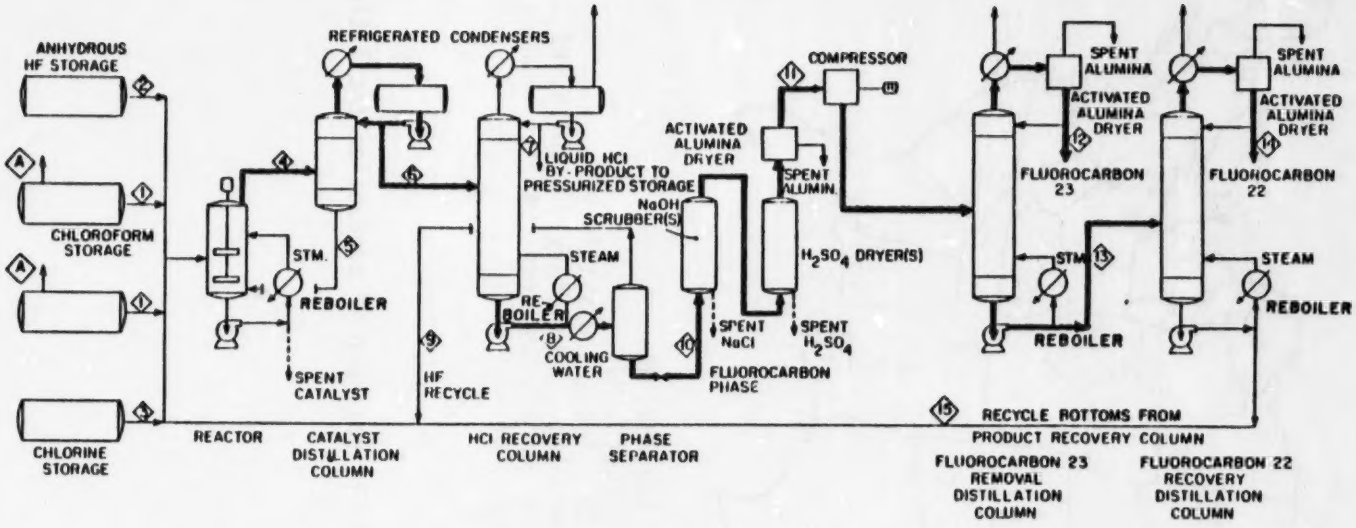
Company	Location
Allied Chemical Corp.	Elizabeth, NJ El Segundo, CA
E.I. duPont de Nemours and Co., Inc.[a]	Louisville, KY Montague, MI
Essex Chemical Corp. (Racon Inc., Subsidiary)	Wichita, KS
Kaiser Aluminum and Chemical Corp.	Gramercy, LA
Pennwalt Corp.	Calvert City, KY

[a] Only the duPont facility at Louisville routinely manufactures fluorocarbon 22; the company's Montague plant can produce fluorocarbon 22 on a nonroutine basis.[5]



1. Allied Chemical Corp., El Segundo, CA
2. Allied Chemical Corp., Elizabeth, NJ
3. E.I. duPont de Nemours & Co., Inc., Louisville, KY
4. Essex Chemical Corp. (Racon, Inc., subsidiary), Wichita, KS
5. Kaiser Aluminum and Chemical Corp., Gramercy, LA
6. Pennwalt Corp., Calvert City, KY

Figure 6-1. Locations of fluorocarbon 22 production facilities


ANHYDROUS HF STORAGE
CHLOROFORM STORAGE
CHLORINE STORAGE
A
A
1
1
2
3
REACTOR
STM.
REBOILER
SPENT CATALYST
4
5
CATALYST DISTILLATION COLUMN
REFRIGERATED CONDENSERS
6
7
LIQUID HCl BY-PRODUCT TO PRESSURIZED STORAGE
STEAM
REBOILER
8
COOLING WATER
9
HF RECYCLE
HCl RECOVERY COLUMN
PHASE SEPARATOR
10
NaOH SCRUBBER(S)
SPENT NaCl
FLUOROCARBON PHASE
ACTIVATED ALUMINA DRYER
SPENT ALUMIN.
H2SO4 DRYER(S)
SPENT H2SO4
11
COMPRESSOR
SPENT ALUMINA
ACTIVATED ALUMINA DRYER
12
FLUOROCARBON 23
STM
13
REBOILER
SPENT ALUMINA
ACTIVATED ALUMINA DRYER
14
FLUOROCARBON 22
STEAM
REBOILER
15
RECYCLE BOTTOMS FROM PRODUCT RECOVERY COLUMN
FLUOROCARBON 23 REMOVAL DISTILLATION COLUMN
FLUOROCARBON 22 RECOVERY DISTILLATION COLUMN

NOTE: The numbers in this figure refer to process streams, as discussed in the text, and the letters designate process vents. The heavy lines represent final product streams through the process.

Figure 6-2. Basic operations that may be used in fluorocarbon 22 production.[7]

Vapor from the reactor (Stream 4) is fed to a distillation column, which removes as overheads hydrogen chloride (HCl), the desired fluorocarbon products, and some HF (Stream 6). Bottoms containing vaporized catalyst, unconverted and underfluorinated species, and some HF (Stream 5) are returned to the reactor. The overhead stream from the column (Stream 6) is condensed and pumped to the HCl recovery column.[7]

Anhydrous HCl byproduct (Stream 7) is removed as overheads from the HCl recovery column, condensed, and transferred to pressurized storage as a liquid. The bottoms stream from the HCl recovery column (Stream 8) is chilled until it separates into two immiscible phases: an HF phase and a denser fluorocarbon phase. These are separated in a phase separator. The HF phase (Stream 9), which contains a small amount of dissolved fluorocarbons, is recycled to the reactor. The denser phase (Stream 10), which contains the fluorocarbons plus trace amounts of HF and HCl, is allowed to evaporate and is ducted to a caustic scrubber to neutralize the HF and HCl. The stream is then contacted with sulfuric acid and subsequently with activated alumina to remove water.[7]

The neutralized and dried fluorocarbon mixture (Stream 11) is compressed and sent to a series of two distillation columns. Overfluorinated material, fluorocarbon 23, is removed as an overhead stream in the first column (Stream 12) and fluorocarbon 22 is recovered as an overhead stream in the second column (Stream 14).[7]

There are a number of process variations in fluorocarbon production. HF may be separated from product fluorocarbons prior to hydrogen chloride removal. Processes may also differ at the stage at which fluorocarbon 22 is separated from fluorocarbon 23: the coproduct fluorocarbons can be separated by distillation and then cleaned separately. Fluorocarbon 23 may be vented rather than recovered. The HCl removal system can vary with respect to the method of removal and the type of byproduct acid obtained. After anhydrous HCl has been obtained as shown in Figure 6-2, it can be further purified and absorbed in water. Alternatively, the condensed overhead from catalyst distillation (Stream 6), can be treated with water to recover an aqueous solution of HCl contaminated with HF and possibly some fluorocarbons. In this case, phase separation HF recycle is not carried out. This latter procedure is used at many older plants in the industry.[7]

CHLOROFORM EMISSIONS AND CONTROLS

Identified sources of chloroform emissions at fluorocarbon 22 production facilities include losses from storage of chloroform feedstock and process fugitive emissions from sources such as process valves, pumps, compressors and pressure relief valves.[9]

None of the three process emissions identified in Figure 6-2 is a major source of chloroform. A vent on the hydrogen chloride recovery column accumulator purges noncondensibles and small amounts of inert gases entering the system with the chlorine gas. While data are not available on the emissions from this source, potential volatile organic emissions are expected to consist of low boiling azeotropes of highly fluorinated ethanes and methanes formed in the fluorination reactor. Vents on the product recovery distillation columns emit only fluorocarbons 22 and 23.[7]

Emission Factors

Table 6-2 presents estimated emission factors for fluorocarbon 22 production facilities. In the current analysis, these factors were used only when plant-specific data were not available.

Current Emissions and Controls

Table 6-3 summarizes estimated current chloroform emissions from fluorocarbon 22 production facilities. Tables 6-4 through 6-9 provide derivation and sources as well as available control information and vent parameters for individual facilities. Where not available for existing storage emissions, vent parameters were taken from previous studies.[13,14] Plant-specific fugitive emission estimates were available only for the two Allied plants. Since Allied/El Segundo, CA, is the smallest fluorocarbon 22 plant, all other plants were assumed to have fugitive emissions similar to Allied/Elizabeth, NJ.

TABLE 6-2. CONTROLLED AND UNCONTROLLED CHLOROFORM EMISSION FACTORS FOR A HYPOTHETICAL FLUOROCARBON 22 PRODUCTION FACILITY[a]

Emission source	Source designation[b]	Uncontrolled chloroform emission factor[c]	Available control technique (ACT)	Percent reduction	Controlled chloroform emission factor
Storage	A	0.59[e] to 2.5[f] kg/Mg	Refrigerated condenser, or	95	0.03 to 0.125 kg/Mg
			High pressure conservation valve and vapor balance	100	0 kg/Mg
Fugitive		--	--	--	<0.023 kg/hr[g]

---

[a] Any given fluorocarbon production plant may vary in configuration and level of control from this hypothetical facility.

[b] Letters refer to vents designated to Figure 6-2.

[c] Emission factors in terms of kg/Mg refer to kilogram of chloroform per megagram of fluorocarbon 22 produced. In cases where a particular source designation applies to multiple operations, these factors represent combined emissions for all, not each, of these operations within the hypothetical facility.

[d] For the refrigerated condenser applied to storage emissions, the ACT removal efficiency is based on an assumed uncontrolled emission temperature of 20°C and a condenser operating temperature of -35°C. Use of a high pressure conservation vent and vapor balance has been reported by one facility with an associated efficiency of essentially 100 percent.[4]

[e] Reference 4.

[f] Reference 7.

[g] Fugitive emission rate is independent of plant capacity. For this reported controlled fugitive emission rate, the associated control technique was not presented. A controlled emission rate of <0.0052 kg/hr has been reported for another facility.[4]

TABLE 6-3. CHLOROFORM EMISSIONS FROM FLUOROCARBON 22 PRODUCTION FACILITIES

		Chloroform emissions (kg/yr)					
		Storage		Fugitive[a]	Total		
Company	Location	Current	Controlled	Current	Current	Controlled	Reduction
Allied	Elizabeth, NJ	7,200	360	200	7,400	560	6,840
Allied	El Segundo, CA	0	--[a]	45	45	45	--
DuPont	Louisville, KY	21,500	2,400	200	21,700	2,600	19,100
Racon	Wichita, KS	9,500	475	200	9,700	675	9,025
Kaiser	Gramercy, LA	930	930[a]	200	1,130	1,130	--
Pennwalt	Calvert City, KY	10,000	500	200	10,200	700	9,500
TOTAL		49,130	4,665	1,045	50,175	5,710	44,465

[a] No controls applied.

TABLE 6-4. EMISSION SUMMARY FOR ALLIED/ELIZABETH, NJ

Company: Allied
Location: Elizabeth, NJ
Latitude: 40° 40' 45" Longitude: 74° 13' 51"

Source	Control technique	Chloroform emission rate (kg/yr)	Vent height (m)	Vent diameter (m)	Discharge temp. (°K)
CURRENT EMISSIONS					
Storage	Conservation vent[a]	7,200[a]	6.1	0.052	283[a]
Fugitive	None	200[a]			
AVAILABLE CONTROL TECHNIQUE					
Storage	ACT	360	15	0.025	238
Fugitive	None	200			

[a] Reference 4.

TABLE 6-5. EMISSION SUMMARY FOR ALLIED/EL SEGUNDO, CA

Company: Allied
Location: El Segundo, CA
Latitude: 33° 56' 38" Longitude: 118° 26' 35"

Source	Control technique	Chloroform emission rate (kg/yr)	Vent height (m)	Vent diameter (m)	Discharge temp. (°K)
CURRENT EMISSIONS					
Storage	High pressure conservation vent[a]	0[a]	--	--	--
Fugitive	None	45[a]			
AVAILABLE CONTROL TECHNIQUE					
Storage	Existing	0	--	--	--
Fugitive	None	45			

[a] Reference 4.

TABLE 6-6. EMISSION SUMMARY FOR DUPONT/LOUISVILLE, KY

Company: DuPont
Location: Louisville, KY
Latitude: 38° 11' 51" Longitude: 85° 54' 13"

Source	Control technique	Chloroform emission rate (kg/yr)	Vent height (m)	Vent diameter (m)	Discharge temp. (°K)
CURRENT EMISSIONS					
Storage[a]	Vented to a common refrigerated condenser (55 percent)	21,500	9.1	0.038	273
Fugitive	None	200			
AVAILABLE CONTROL TECHNIQUE					
Storage	ACT	2,400	15	0.025	238
Fugitive	None	200			

[a] Reference 6.

TABLE 6-7. EMISSION SUMMARY FOR RACON/WICHITA, KS

Company: Racon
Location: Wichita, KS
Latitude: 37° 43' 30" Longitude: 97° 20' 00"

Source	Control technique	Chloroform emission rate[a] (kg/yr)	Vent height (m)	Vent diameter (m)	Discharge temp. (°K)
CURRENT EMISSIONS					
Storage	None	4,750 4,750	6.1 6.1	0.052 0.052	300 300
Fugitive	None	200			
AVAILABLE CONTROL TECHNIQUE					
Storage	ACT	475	15	0.025	238
Fugitive	ACT	200			

[a] Emission rates based on Racon's estimate of total emissions at 9,700 kg/yr,[10] assuming 200 kg/yr to be fugitive emissions. Storage emissions were apportioned between two tanks with model plant parameters.

TABLE 6-8. EMISSION SUMMARY FOR KAISER/GRAMERCY, LA

Company: Kaiser
Location: Gramercy, LA
Latitude: 30° 03' 25" Longitude: 90° 40' 13"

Source	Control technique	Chloroform emission rate (kg/yr)	Vent height (m)	Vent diameter (m)	Discharge temp. (°K)
CURRENT EMISSIONS					
Storage[a]	Refrigerated condenser (95 percent)	930	15	0.025	238
Fugitive		200			
AVAILABLE CONTROL TECHNIQUE					
Storage	Existing	930	15	0.025	238
Fugitive	None	200			

[a] Reference 11.

TABLE 6-9. EMISSION SUMMARY FOR PENNWALT/CALVERT CITY, KY

Company: Pennwalt

Location: Calvert City, KY

Latitude: 37° 03' 10" Longitude: 88° 19' 40"

Source	Control technique	Chloroform emission rate (kg/yr)	Vent height (m)	Vent diameter (m)	Discharge temp. (°K)
CURRENT EMISSIONS					
Storage	None	10,000[a]	6.1	0.052	300
Fugitive	None	200			
AVAILABLE CONTROL TECHNIQUE					
Storage	ACT	500	15	0.025	238
Fugitive	None	200			

[a] Reference 12.

Available Control Techniques

Available control techniques (ACT) were assessed for storage and fugitive emissions. For storage emissions, ACT was determined to be a refrigerated condenser with 95 percent control efficiency. The estimated 95 percent control of storage emissions is based on the theoretical proportionality of emission control to vapor pressure reduction with a 20°C ambient temperature and -35°C condenser outlet temperature. Refrigerated condensation was chosen mainly because it is the principal control currently in use for halogenated chemical storage. Condensers are used at six of the seven currently controlled chloroform storage facilities cited in this chapter and Chapter 5. One fluorocarbon 22 plant (Allied/El Segundo, CA) uses pressurized storage. Although the size of this tank is not known, available production and emissions data indicate that it is at the smallest fluorocarbon 22 plant and that the tank is quite small relative to those at other plants. Since pressurized storage is only a practical control alternative for small fixed-roof tanks, it is not applicable to the larger plants. Refrigerated condensation can be applied to existing fixed roof chloroform storage tanks without taking them out of operation, a factor which may be critical for installation of controls at the three fluorocarbon 22 plants which have only one chloroform storage tanks.

Other options for control of emissions from storage of volatile organic compounds include: (1) rim-mounted secondary seals or fixed roofs on external floating roof tanks, (2) internal floating roofs on fixed roof tanks, (3) rim-mounted secondary seals or contact internal floating roofs for noncontact internal floating roof tanks, (4) liquid-mounted primary seals on contact internal floating roofs, (5) rim-mounted secondary seals on contact internal floating roofs, (6) carbon adsorption, (7) thermal oxidation, and (8) pressure vessels. Option 1 does not apply to this case because external floating roofs are not used for organic chemical storage (they are genrally used only on large tanks for petroleum liquids). Options 2, 3, 4, and 5 involve various configurations of internal floating roofs. Although floating roofs can provide control comparable to refrigerated condensers, chloroform's ability to dissolve rubber floating roof components would be a problem for typical floating roofs. Use of special materials may overcome this problem, but lack of industry experience and information on potential rubber substitutes prevented further consideration of these options. The need to empty and clean tanks for floating roof installation could also be a constraint at plants without available alternative storage.

Carbon adsorbers (Option 6) are not known to be used for control of emissions from storage of organic chemicals, although they can provide comparable control. Installation and operation of carbon absorbers is considerably more complex than for condensers. Adsorbers are likely to require significantly more operating labor or more sophisticated instrumentation to ensure efficient desorption cycles under fluctuating input conditions. Provision of cooling water and steam or vacuum for regeneration may be a consideration in the vicinity of existing tanks. Disposal of cooling water, condensate and spent carbon are additional considerations which are not encountered with condensers. Thermal oxidation (Option 7) is not a preferred option for chloroform emissions alone, because chloroform is nonflammable and would require auxiliary fuel or joint control of more combustible hydrocarbons for effective control. In addition, no chloroform recovery is possible with thermal oxidation. As stated above, pressure vessels (Option 8) are not practical for the size of storage tanks used at all but the smallest fluorocarbon 22 production plant. Use of pressure vessels would also require abandoning existing fixed-roof tanks and building new pressure vessels, which would be very expensive relative the add-on control options discussed above.

Fugitive chloroform emissions from fluorocarbon 22 production could potentially be reduced by instituting a control program involving inspections, repair and equipment specifications. These fugitive emissions are believed to be quite small, however, estimated at 200 kg/yr or less for each plant, and less than four percent of total potential emissions at any plant. For this reason, ACT was not applied to process fugitive emissions.

The estimated ACT storage control efficiency of 95 percent was applied to emissions estimated for currently uncontrolled chloroform storage at fluorocarbon 22 production facilities, including Allied/Elizabeth, NJ, Racon/Wichita, KS, and Pennwalt/Calvert City, KY. The 95 percent control was also applied at DuPont/Louisville, KY, where the level of existing control is only 55 percent (See Table 6-6). ACT did not apply to Kaiser/Gramercy, LA, because 95 percent control will shortly be installed there. Pressurized storage at Allied/El Segundo, CA, eliminates storage emissions entirely. Of the four plants which would install refrigerated condensers on their storage tanks, DuPont/Louisville, KY would achieve the greatest reduction over current chloroform emissions (about 19 Mg/yr). Note that this reduction consists of the difference between current 55 percent control and 95 percent at ACT. Pennwalt/Calvert City, KY and Racon/Wichita, KS would control 9.5 and 9 Mg/yr respectively; Allied/Elizabeth, NJ would reduce emissions by about 6.8 Mg/yr. This results in a national emission reduction of about 44.4 Mg/yr. Current emissions, controlled emissions, and emission reductions are summarized in Table 6-3. Vent parameters for the refrigerated condensers used in ACT for chloroform storage include their -35°C (238°K) outlet temperature, with height and diameter (15 and 0.025 meters) taken from a previous vent parameter estimate.[14]

CONTROL COSTS

Table 6-10 presents estimated costs of control on chloroform storage at the four fluorocarbon 22 plants to which ACT applies. The ACT condenser would be sized to handle the maximum expected emission rate, which would occur when chloroform being loaded into the bulk storage tank displaces air and vapor in the headspace. The displacement rate would be the same as the maximum chloroform loading rate. A worst case would involve saturation conditions in the headspace, at ambient temperatures.

The available information on production, chloroform storage and loading rates at fluorocarbon 22 plants is summarized in Table 6-11. For control cost estimation, it was assumed that the Pennwalt and Racon plants would have chloroform load-in rates similar to the 5,000 gallon/hr maximum rate reported for Allied/Elizabeth, and that loading capacities at DuPont/Louisville would

TABLE 6-10. CONTROL COSTS FOR CHLOROFORM STORAGE AT FLUOROCARBON 22 PLANTS

	Allied/ Elizabeth, NJ	DuPont/ Louisville, KY	Racon/ Wichita, KS	Pennwalt/ Calvert City, KY	Total
Base capital cost	$45,000	$ 75,000	$45,000	$45,000	$210,000
Installed capital cost	$92,400	$154,000	$92,400	$92,400	$431,200
Annualized capital cost	$26,800	$ 44,700	$26,800	$26,800	$125,100
Utilities	1,900	6,100	1,900	1,900	11,800
Operating labor	3,900	3,900	3,900	3,900	15,600
Annual cost	$32,600	$ 54,700	$32,600	$32,600	$152,500
Recovery credit	(4,600)	(13,000)	(6,100)	(6,500)	(30,200)
Net annual cost	$28,000	$ 41,700	$26,500	$26,100	$122,300
Emission reduction (Mg/yr)	6.8	19.1	9.0	9.5	44.4
Cost effectiveness ($/Mg)	4,100	2,200	2,900	2,700	2,800

[a] Costs in July 1982 dollars.

TABLE 6-11. BACKGROUND DATA FOR CONTROL COST ESTIMATES

Company and location	Total CFC production capacity[a] (Mg/yr)	Fluorocarbon 22 production (Mg/yr)	Uncontrolled chloroform storage emissions[b] (kg/yr)	Maximum chloroform load-in rate (gallons/hr)
Allied	181,000			
Elizabeth, NJ		12,100[c]	7,200	5,000[d]
El Segundo, CA		2,600[c]	0	3,500[f]
DuPont	227,000			
Louisville, KY		45,000[g]	47,800[g]	NA
Racon	20,000			
Wichita, KS		NA	9,700	NA
Kaiser	30,000			
Gramercy, LA		NA	18,600[h]	NA
Pennwalt	36,000			
Calvert City, KY		NA	10,000	NA

[a] Reference 3. Includes production of all chlorofluorocarbons by each company.

[b] See Tables 6-4 through 6-9.

[c] Reference 4.

[d] Tank car load-in at 3,500 gallons/hr and tank truck load-in at 1,500 gallons/hr; Reference 4.

[e] Pressurized tank with negligible emissions; Reference 4.

[f] Tank car load-in at 3,500 gallons/hr only; Reference 4.

[g] Estimated from information in Reference 6.

[h] Reference 11.

NA = not available.

be about four times this rate, or 20,000 gallons/hr. These assumptions were based on the relative reported emissions for these plants. The estimated production capacity of the DuPont plant was also considered.

Base capital costs for refrigerated condenser systems to handle the above loading rates would be about $45,000 for 5,000 gallons/hr and $75,000 for 20,000 gallons/hr. These estimates are based on costs provided by an equipment manufacturer for the flow rates, cooling rates and -35°C operating temperature required to achieve 95 percent control of storage emissions.[15] Additional allowances of 18 percent of base cost for taxes, freight and instrumentation and 74 percent for installation[16] result in the installed capital costs in Table 6-10. A previous cost analysis for refrigerated condensers estimated an overall annualized captial cost factor of 29 percent, which includes maintenance labor and material (6 percent), taxes, insurance and administration (5 percent) and a capital recovery factor (18 percent).[7] Applying this factor results in the annualized capital costs in Table 6-10.

The condensers under consideration are air-cooled, so utilities consist of electricity for the compressor and fan. The approximate utility costs in Table 6-10 were based on an estimated $0.08/kWh electric rate,[18] assuming condenser operation at full capacity during loading and consumption at 15 percent of full-capacity during idling.[15] Loading was assumed to occur 10 percent of the time, based on actual data for Allied/Elizabeth (902 hrs/yr).[4] Thus total condenser operating time was estimated at 2060 hrs/yr. The condenser sized for 5,000 gallon/hr loading rate would consume about 11.5 kW/hr.[15] The unit for the 20,000 gallon/hr loading rate would be about 20 percent more efficient per gallon loaded, and thus would use about 37 kW/hr. Operating labor is relatively constant regardless of condenser size, and has been estimated at 10 percent of condenser operating time.[19] Ten percent of the estimated operating time cited above and a labor rate of $19/hr,[17] result in an annual labor cost of about $3900.

Recovery credits are based on emission reductions from Table 6-3. Recovery credits are based on the July 1982 price for chloroform, $682/Mg ($0.33/lb).[20]

All above costs are in July 1982 dollars. Costs in original references were inflated to July 1982 using the Chemical Engineering plant cost index,[21] except the electric utility rate for July 1982, which was projected from available rate data.[18]

COST-EFFECTIVENESS

Table 6-10 provides estimated cost-effectiveness of the storage controls specified as available control techniques in the previous section. For individual plants, these controls are estimated to cost from $2,200 to $4,100 per megagram of chloroform controlled, with an industry-wide average of $2,800 per megagram.

CONCLUSIONS

With 95 percent control of storage emissions at the four fluorocarbon 22 plants which do not currently have that level of control, total chloroform emissions from this source category can be reduced from about 50 Mg/yr to about 5.7 Mg/yr, at a total annual cost of $122,300. This annual cost includes a chloroform recovery credit of $30,200 and a pre-recovery cost of $152,000. Overall cost-effectiveness of available control techniques is estimated at $2,800 per megagram.

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7. OXYBISPHENOXARSINE/1,3-DIISOCYANATE MANUFACTURE

INTRODUCTION

Oxybisphenoxarsine (OBPA) and 1,3-diisocyanate are produced by Aerojet General Corporation in Sacramento, California. OBPA is a fungicide that is combined with rubber to prevent mold growth on gaskets and seals. 1,3-Diisocyanate is an intermediate in the production of polyurethane resins. Both the OBPA and diisocyanate processes use chloroform as a solvent. A third source of chloroform emissions from the Aerojet facility is a deep well deaerator. All three sources are described separately below.

OXYBISPHENOXARSINE

The Chemical Operations Division of Aerojet General Corporation is the only producer of oxybisphenoxarsine. For this reason, much of the information on the production of OBPA is limited and believed to be proprietary. It is known that chloroform acts as a carrier solvent for OBPA.

On November 29, 1982, Aerojet received a permit to construct an activated carbon system to reduce chloroform emissions at the OBPA facility from 635 kg/day to 30 kg/day (95 percent control). The carbon adsorption unit is a Series 500 System manufactured by VIC Manufacturing Company. Although Aerojet estimated 95 percent control and this level is used in emission estimates, preliminary data supplied by the County of Sacramento Air Pollution Control District indicate the system may be achieving 98 percent control.[1] Chloroform emissions and stack parameters from the OBPA process are reported in Table 7-1.[2]

1,3-DIISOCYANATE

Like OBPA, little information is known about the Aerojet 1,3-diisocyanate process. From other sources it is known that carbon tetrachloride can be used as an absorbent in a scrubber which is part of a phosgene/isocyanate process in West Virginia and Texas.[3,4] Because little information was available on the Aerojet process, it can be surmised that this is how chloroform is used.

TABLE 7-1. CHLOROFORM EMISSION DATA FOR AEROJET GENERAL CORPORATION

	Source locations			Stack characteristics			
	Universal Transverse Mercator (UTM) Coordinate		Emission rate,	Height,	Diameter,	Velocity,	T,
Source	E	N	grams/second (pounds/day)	meters	meters	meters/ second	°K
Deep well deaerator	653.43	4273.30	0.81 (50)	3.96	0.04	0.34	285.0
OBPA Facility	655.28	4274.72	0.66 (65)	4.75	0.63	2.98	285.0
1,3-Diisocyanate Facility[a]	655.22	4275.36	0.25 (18)	6.10	0.40	0.36	285.0

[a] This source operates only 9 hours per day.

It is known that chloroform sources from 1,3-diisocyanate production at Aerojet include the acid chloride area scrubber columns, the process area scrubber column, the azide abatement area scrubber column, the Nash vacuum system circulation vessels, the high vacuum still area knockout pot, and the chloroform recycle area knockout pot. These sources are routed to an inlet duct of the chloroform recovery system. The chloroform recovery system is a carbon adsorber recently installed by VIC Manufacturing Company. Emission rates and stack parameters from the 1,3-diisocyanate process are reported in Table 7-1.[2]

DEAERATION

The design purpose of a vacuum deaerator is to remove the corrosion contributing noncondensable gases from water, namely oxygen, nitrogen, and carbon dioxide prior to deep well injection. Because volatile organics, such as chloroform, have a limited solubility in water, a portion of these materials are also removed from the deaeration process. Sources of chloroform that supply aqueous waste to the deaeration system include both the OBPA and the diisocyanate facility.

Aerojet estimates chloroform emissions from the deep well deaeration facility amount to 22.7 kg/day. There are no controls on this facility. Stack parameters are shown in Table 7-1.[2]

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8. PHARMACEUTICAL AND VITAMIN C PRODUCTION

This chapter presents the results of a recent survey of domestic pharmaceutical manufacturers' chloroform usage and disposal, as well as a summary of chloroform usage and emissions at one facility producing Vitamin C.

PHARMACEUTICAL PRODUCTION

Chloroform is one of many solvents used in the manufacture of synthetic pharmaceuticals. Pharmaceuticals are typically made in a series of batch operations, many of which can involve the use of solvents. These operations include reactors, distillations, filters, extractors, centrifuges, crystallizers, dryers and various holding tanks. Solvent emissions can occur in any of these process steps, and can also occur from solvent storage, transfer, and recovery systems. Solvents may be used as a reaction medium, to dissolve an intermediate product prior to a process step, to wash an intermediate or final product, or as a drier after a water-based production step.[1] Except for the Vitamin C production process described later in this chapter, no information is available on specific locations, applications, or emission points for chloroform use in the pharmaceutical industry.

The Pharmaceutical Manufacturer's Association conducted a survey of solvent use by member companies in May 1984.[2] The chloroform purchase, emission and disposal statistics provided by this survey are as follows:

Annual chloroform purchase	1150 Mg
Direct air emissions	575 Mg
Sewer	150 Mg
Incineration	100 Mg
Contract haul	50 Mg
Other disposal or loss	250 Mg

Respondents to this survey account for about half of the 1982 domestic sales of ethical pharmaceuticals, so actual chloroform usage and loss rates are significantly higher than the responses totalled above. However, it is believed that some surveyed manufacturers may not have responded because they do not use the subject solvents. Thus doubling the above responses would probably result in overestimation of true chloroform usage and losses. The "other disposal or loss" category may include off-site solvent recovery, deep-well injection, lab-pack disposal by outside vendors and undetermined losses.

From these statistics, it appears that roughly 1,000 Mg/yr of chloroform may be emitted directly to the air by pharmaceutical manufacturers, with some significant indirect atmospheric losses from chloroform disposed of in sewers. This total includes the emissions from the Vitaminc C production process described in the next section. The survey cited did not provide any locations or other company or plant-specific details.

VITAMIN C PRODUCTION

Source Description

Chloroform is used as a solvent in the manufacture of crude ascorbic acid (Vitamin C). The starting material for ascorbic acid is dextrose, which is hydrogenated to sorbitol, fermented, and crystallized into sorbose. The sorbose is then slurried in a solvent reactor, followed by mixture with acid and then neutralized. Following this the material is oxidized and dried, forming diacetone gulosonic acid (DAG). The DAG is slurried with chloroform, followed by a rearrangement to form crude ascorbic acid. The ascorbic acid is filtered from the chloroform-containing mother liquor, crystallized, dried, and shipped out as a final product.[3]

Source Locations

There are two producers of Vitamin C in the U.S., Hoffman-LaRoche, Belvidere, New Jersey, and Pfizer, Groton, Connecticut. The Hoffman-LaRoche plant has a capacity of 30 million pounds per year, while the smaller Pfizer plant has a capacity of 2 million pounds per year.[4] The remainder of this discussion will address only the Hoffman-LaRoche plant, since detailed information was not gathered for the Pfizer plant.

Chloroform Emissions and Controls

Potential chloroform emission sources in the Hoffman-LaRoche Vitamin C production include: fugitive losses from process equipment and solvent recovery equipment; vent emissions from the carbon adsorber used to control process, recovery system and storage tank vents; an uncontrolled chloroform storage tank; inadvertent spills of solvent or process materials; and vaporization from wastewater and cooling water. Recent estimates for these emissions are as follows:[5]

Fugitive	116 Mg/yr
Carbon adsorber vent	78 Mg/yr
Storage tank	6 Mg/yr
Spills	10 Mg/yr
Wastewater/cooling water	13 Mg/yr
Total	223 Mg/yr

The current carbon adsorber is estimated to provide 78 percent control of ducted emissions from a large number of process unit vents, the solvent recovery unit condensers, and three of the four storage tanks. Plans exist to continue upgrading of this adsorber, by improving post-regeneration drying and use of a gas chromatograph for better timing of the desorption cycle. A realistic future control level of 95 percent is projected.[6] This would result in carbon adsorber vent emissions of less than 20 Mg/yr, compared to the current 78 Mg/yr cited above.

Control Costs

The initial cost of the carbon adsorber itself was $34,500 in 1978, with additional installation costs of $500,000 in 1981, and an upgrading of the system in 1983 for $131,000. Current annual operating costs are estimated at $40,000 for steam, $13,500 for maintenance, and $53,500 for operating labor. The value of the recovered solvents is estimated at $218,000 per year.[3]

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9. TRICHLOROETHYLENE PHOTODEGRADATION

SOURCE DESCRIPTION

Trichloroethylene (TCE) is a synthetic organic chemical used almost exclusively (>90 percent) in degreasing operations. The chemical has become pervasive in the environment due to fugitive emissions during production, use, and disposal.

Production of trichloroethylene has been declining since the early 1970's. Production of trichlorethylene has fallen from 206,000 Mg in 1973 to 109,000 in 1982.[1,2] This trend is expected to continue through 1987 with a 0 to 3 percent annual decline through the period.[2]

Only two sites in the U.S. manufacture trichloroethylene: Dow Chemical in Freeport, Texas and PPG Industries in Lake Charles, Louisiana. Releases from production are only a small part of the total released each year.

Trichloroethylene uses include solvent degreasing, miscellaneous solvent uses including the production of funigicides, cleaning fluids, and adhesives, and as a chain terminator in polyvinyl chloride manufacture. Approximately 22 percent of all trichloroethylene manufactured is exported.[2]

Almost all TCE production is ultimately released to the environment, except for 6 percent which is consumed as a feedstock or destroyed by incineration. During or following use, as much as 79 percent of production is released to air, 14 percent to land, and 1 percent to ambient waters.[1] Once airborne, trichloroethylene remains in the troposphere until it reacts with hydroxyl free radicals (·OH), the principal scavenging mechanism for trichloroethylene and most other halogenated compounds. Decomposition products include dichloroacetyl chloride, phosgene, carbon monoxide, chloroform, hexachlorobutene, and hydrochloric acid. The estimated residence time for trichloroethylene in the atmosphere ranges from 11 to 15 days.[3,4]

Laboratory experiments have demonstrated the photochemical formation of chloroform from trichloroethylene.[5] In one study, synthetic mixtures of trichloroethylene, nitrogen dioxide, water vapor, and a hydrocarbon mixture were irradiated by a bank of fluorescent lamps designed to simulate the intensity and spectral distribution of light prevailing in the lower troposphere. The hydrocarbon mixture was a typical gasoline consisting of 60 percent paraffins, 13 percent olefins, and 27 percent aromatics. Approximately 2 hours after initiation of the experiment, chloroform formation began. After 48 hours, approximately 7 ppb of chloroform was formed (Figure 9-1). Phosgene was measured at a level slightly lower than chloroform. Dichloroacetyl chloride and HCl were both measured during the experiment, but the concentration could not be measured because of the procedures employed.

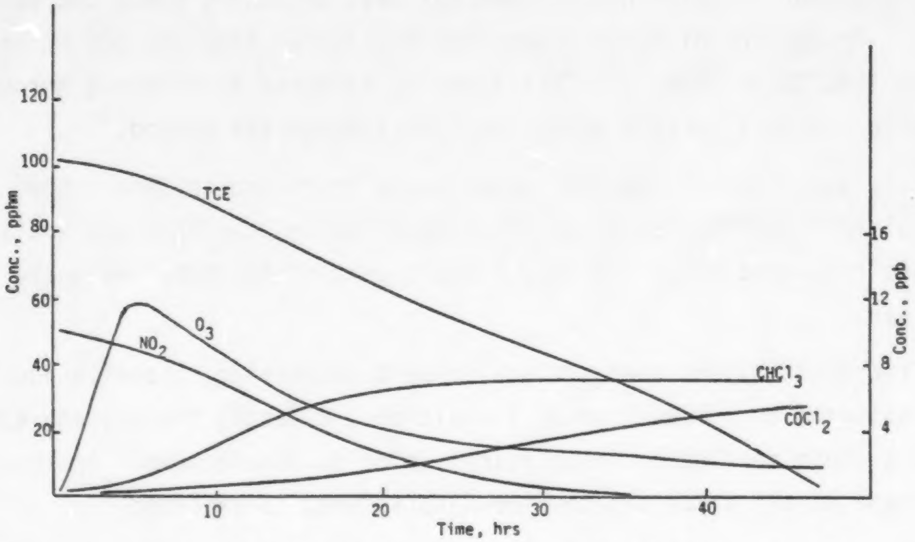

Figure 9-1. Chloroform formation due to photochemical decomposition of trichloroethylene.

The following reaction mechanism is believed to account for the observed formation of the products mentioned above. The mechanism involves a chlorine-sensitized photo-oxidation of trichloroethylene. The mechanism accounts for the products and the time lag in the experiment mentioned above. Time is required for the initial propagation of chlorine radicals, oxygen radicals, and other radical species. The mechanism believed to account for the formation of chloroform from trichloroethylene is as follows:

1) $C_2HCl_3 \xrightarrow{hv} C_2HCl_2 + Cl\cdot$
2) $Cl\cdot + C_2HCl_3 \longrightarrow C_2HCl_4\cdot$
3) $C_2HCl_4\cdot + O_2 \longrightarrow C_2HCl_4O_2\cdot$
4) $C_2HCl_4\cdot + C_2HCl_4O_2\cdot \longrightarrow C_2HCl_4O_2C_2HCl_4$
5) $C_2HCl_4O_2\cdot + C_2HCl_4O_2\cdot \longrightarrow 2C_2HCl_4O\cdot + O_2$
6) $C_2HCl_4O\cdot \longrightarrow CHClCOCl_2 + Cl\cdot$
7) $C_2HCl_4O \longrightarrow COCl_2 + CHCl_2\cdot$
8) $CCl_3CHClO\cdot \longrightarrow CCl_3\cdot + HCl + CO$
9) $CCl_3\cdot + O_2 \longrightarrow COCl_2 + Cl\cdot$
10) $CHCl_2\cdot + Cl\cdot \longrightarrow CHCl_3$

As stated above, 109,000 Mg of trichloroethylene was produced in 1982. Subtracting exports and assuming that 79 percent of trichloroethylene produced enters the atmosphere, 67,200 Mg were released to the atmosphere. As shown in Figure 9-1, for every ppm of trichloroethylene in the atmosphere, 7 ppb of chloroform is formed, or of the 67,200 Mg of trichloroethylene released, 420 Mg of chloroform is formed. Secondary formation of chloroform from trichloroethylene photodegradation is unlikely to cause significant ground level concentrations. Maximum concentrations of trichloroethylene in urban atmospheres have been reported to be 3.07 ppb, with average concentrations being approximately 213 ppt.[6] Using the ratio listed above, maximum concentrations of chloroform in urban atmospheres due to trichloroethylene photodegradation would be 21.5 ppt (105 ng/m^3), while average concentrations would be 1.5 ppt (7.3 ng/m^3). This level would account for 0.77 percent of chloroform found in urban atmospheres.[6]

Because chloroform is formed as a secondary by-product of the hydrolysis of trichloroethylene, direct control is not possible. The only possible means of reducing chloroform formation would be to reduce trichloroethylene use further by continued substitution to other halogenated solvents (e.g. 1,1,1-trichloroethane, or methylene chloride), or by use of alternate cleaning methods.

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10. COOLING WATER

In steam electric power generators, cooling water is used to condense steam. Cooling water is often chlorinated to prevent growth of slime-forming organisms, which inhibit the heat exchange process, on heat-exchanger tubes.[1] Chloroform is formed in cooling water from the reaction between chlorine and naturally-occurring organic compounds in the water. About 65 percent of steam electric plants chlorinate to prevent fouling by slime-forming organisms. The remaining plants either do not have a biofouling problem or use a control method other than chlorine.[1]

Two types of cooling water systems are in general use: once-through systems and recirculating systems. Chloroform air emissions occur when chloroform formed in cooling water evaporates to the atmosphere. Chloroform formation and fate in cooling water is discussed below.

SOURCE DESCRIPTION

Once-Through Cooling Systems

In a once-through cooling water system, cooling water is drawn from the water source, passed through the heat exchanger (where it absorbs heat), and returned directly to the water source. Typically, chlorine is added to cooling water periodically for a time period long enough to kill any organisms growing in the heat-exchanger tubes. For example, a large coal-fired electric plant chlorinates cooling water for 30 minutes daily.[2] Chloroform formed in the cooling water is discharged to the source water and evaporates.

Recirculating Cooling Systems

In a recirculating cooling water system, cooling water is withdrawn from the water source and passed through the condensers several times before being discharged to the receiving water. Heat is removed from the cooling water after each pass through the condenser. Three major methods are used for removing heat from recirculating cooling water: cooling ponds or canals;

mechanical draft evaporative cooling towers; and natural draft mechanical cooling towers. Recirculating cooling water typically is chlorinated continuously. The evaporation of water from a recirculating cooling water system in cooling ponds or cooling towers results in an increase in the dissolved solids concentration of the water remaining in the system. Scale formation is prevented in the system by periodically bleeding off a portion of the cooling water (blowdown) and replacing it with fresh water which has a lower dissolved solids concentration.

Industry Capacity

The Department of Energy listed 842 steam electric generating plants in 1978 with a total generating capacity of 453,000 MW.[3] The 1982 generating capacity was estimated to be 567,000 MW, an increase of 25 percent.[4]

CHLOROFORM EMISSIONS

Once-Through Cooling Systems

The amount of chloroform formed in once-through cooling systems can be computed based on the volume of cooling water chlorinated and the chloroform concentration resulting from chlorination. The water volume chlorinated can be computed based on the cooling water flow rate in nuclear and nonnuclear plants practicing chlorination and, because chlorination is intermittent, the amount of time the water is chlorinated.

Approximately 60 percent of nonnuclear steam electric plants use once-through cooling systems. These cooling systems used 2.0×10^{14} liters of water in 1978.[5] Based on the 25 percent increase in power generating capacity estimated above, an estimated 2.5×10^{14} liters were used in 1982.

Because the cooling requirements at nuclear plants are about the same as for coal-fired plants, data from a coal-fired plant can be used to estimate the once-through cooling water volume for nuclear power plants.[6] The average generating capacity of U.S. nuclear power plants is 1,600 MW.[3] The cooling water volume at a similar-sized (1,700 MW) coal-fired plant is 5.55×10^9 liters/day.[1] Based on the ratio of generating capacities, a 1,600 MW nuclear power plant requires 5.1×10^9 liters/day. The eleven nuclear plant once-through systems, therefore, use approximately 2.0×10^{13} liters/year of cooling water.[7]

The total cooling water volume in once-through systems, 2.7 x 10^{14} l/yr, is the sum of cooling water volumes in nuclear and nonnuclear steam electric plants. Based on the example cited above, once-through systems are estimated to chlorinate daily for 0.5 hour, or 2.1 percent of the operating time.[2] Thus, assuming 65 percent of once-through cooling water is chlorinated 2.1 percent of the time yields a total chlorinated volume of 3.7 x 10^{12} liters per year. Using a measured 20.5 μg/l chloroform concentration in a once-through cooling system as a basis, an estimated total of 75.9 Mg/year of chloroform are produced in all once-through systems from chlorination.[8] The entire amount would evaporate to the atmosphere.

Recirculating Cooling Systems

The amount of chloroform produced in recirculating cooling systems can be estimated by multiplying the blowdown volume of cooling systems by a published cooling system chloroform production factor. Total chloroform production in recirculating cooling systems has been estimated to be 4.32 x 10^{-7} kg per liter of blowdown for a continuously chlorinating cooling tower, and 6.6 x 10^{-7} kg per liter of blowdown for a cooling tower chlorinating once per week.[9]

Recirculating cooling systems in nonnuclear steam electric plants discharged 3.2 x 10^{11} liters of blowdown in 1978.[10] It is estimated that 4.0 x 10^{11} liters were discharged in 1982, based on a 25 percent increase in generating capacity. Nuclear power plants account for 12 percent of the power generated in the United States.[4] Assuming that nuclear power plants produce an amount of blowdown equal to 12 percent of the nonnuclear blowdown volume, nuclear plants discharge 4.8 x 10^{10} l/yr of blowdown. The total blowdown volume discharged from recirculating cooling systems, 4.5 x 10^{11} l/yr, is the sum of blowdown from nuclear and nonnuclear plants.

Assuming that 65 percent of recirculated cooling water is chlorinated, 2.9 x 10^{11} liters/yr of blowdown are chlorinated. Assuming that all chlorinating cooling towers chlorinate continuously yields an estimate of 125 Mg/yr of chloroform produced. Assuming all chlorinating cooling towers chlorinate intermittently yields an estimate of 191 Mg/yr of chloroform produced. Because most plants chlorinate continuously, the amount of chloroform produced is probably best estimated by the quantity 125 Mg/yr. However, by estimating chloroform production based on the assumption that all systems chlorinate intermittently a reasonable range of potential chloroform emissions can be established. Thus, an estimated 125 to 191 Mg/yr of chloroform are produced in recirculating cooling systems. Virtually all the chloroform formed in recirculating cooling systems evaporates to the atmosphere.

Summary of Chloroform Production

In conclusion, the amount of chloroform produced by chlorination in once-through cooling systems and recirculating systems is calculated to be between 197 and 263 Mg/yr. Seventy-two megagrams are discharged directly to water (then evaporated to the air) by once-through systems, while 125 to 191 Mg/yr are emitted to the air by recirculating systems.

CHLOROFORM CONTROL METHODS

Chloroform emissions can be reduced by using a biofouling control method other than chlorination. Alternatives to chlorination are other oxidizing chemicals, nonoxidizing biocides, and mechanical cleaning.[1] None of these alternatives, however, are used widely at this time.

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9. Reference 2, pp. 700-701.
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11. DRINKING WATER

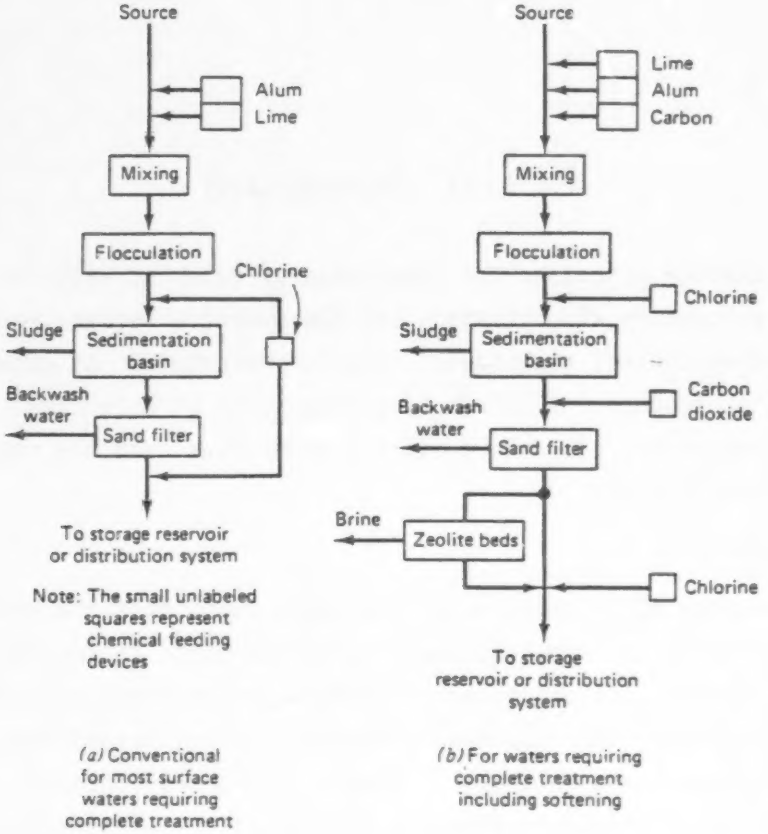
This chapter discusses the importance of drinking water treatment as a source of chloroform air emissions and the potential effectiveness of chloroform formation control techniques. A brief description of water treatment processes is presented, followed by a discussion of chloroform formation, emissions potential, chloroform control techniques, and the cost-effectiveness of control techniques.

SOURCE DESCRIPTION

The purpose of drinking water treatment is to make the water safe and attractive for the consumer by removing contaminants in the raw water. The principal contaminants of concern in most water sources are pathogenic bacteria, turbidity and suspended materials, color, tastes and odor, trace organic compounds, and hardness.[1] Figure 11-1 shows schematic flowsheets for two typical water treatment plants. Sedimentation, preceded by alum addition, mixing, and flocculation, removes a large percentage of suspended materials including bacteria, sediment, and turbidity. Chlorine addition oxidizes certain chemicals and kills pathogenic bacteria. The sand filters remove unsettled floc particles and suspended bacteria. Where needed, carbon powder can remove certain amounts of trace organic compounds.

CHLOROFORM FORMATION

Chloroform is formed during chlorination of drinking water by a complex reaction mechanism between chlorine and organic precursors in raw water. The organic precursors are natural aquatic humic substances such as humic and fulvic acids.[2] Major factors influencing this reaction are the amount and type of precursor material present in raw water, temperature, pH, and chlorine dose.[3] These factors influence both the chloroform formation rate and the terminal chloroform concentration. The reaction rate between chlorine and precursor material is important because the reaction can continue to form


Source
Alum
Lime
Mixing
Flocculation
Chlorine
Sludge
Sedimentation basin
Backwash water
Sand filter
To storage reservoir or distribution system
Note: The small unlabeled squares represent chemical feeding devices
Source
Lime
Alum
Carbon
Mixing
Flocculation
Chlorine
Sludge
Sedimentation basin
Carbon dioxide
Backwash water
Sand filter
Brine
Zeolite beds
Chlorine
To storage reservoir or distribution system

(a) Conventional for most surface waters requiring complete treatment

(b) For waters requiring complete treatment including softening

Figure 11-1. Schematic of typical water treatment plants.[4]

chloroform in water distribution mains long after the water has left the treatment plant. Data show that as much as 87 percent of the chloroform formation potential can remain in the water following treatment.[5] The time-dependent nature of the chloroform formation reaction is an important consideration in evaluating chloroform air emissions and control techniques.

The extent and severity of chloroform in the Nation's drinking water was shown by two surveys conducted by EPA: The National Organics Reconnaissance Survey (NORS) made in 1975 and the National Organics Monitoring Survey (NOMS) made in 1977.[6,7] The NORS analyzed raw and treated water samples from 80 U.S. cities to determine the organic compound content of the water, including chloroform concentrations. The samples were collected and iced for shipment, but not dechlorinated. Thus, the NORS chloroform concentrations in finished drinking water are minima for those locations. The chloroform concentrations in raw water samples ranged from zero to one μg/l. The NOMS analyzed drinking water in 113 U.S. cities, including many of the same cities sampled in the NORS. Both surveys were done prior to the establishment of a maximum contaminant level (MCL) for trihalomethanes, and thus represent the level of contamination generally present before controls. The results of the NORS and NOMS and the 1980 population of the cities where samples were taken are presented in Table 11-1. As shown by the table, chloroform concentrations range from "not detected" to 311 μg/l. Both groundwater and surface water sources were surveyed.

CHLOROFORM EMISSIONS

Chloroform Emissions Potential

Chloroform air emissions result when chloroform in water is transferred to air by evaporation. An experiment has shown that the concentration of chloroform in a cup of stirred water decreased by one-half every 20 minutes.[8] Chloroform formed in drinking water potentially can be emitted at points where the water system is open to the air, such as at the water treatment plant, in open storage reservoirs for treated water, at the consumer's tap, and in the sewerage system. Because the transfer rate of chloroform from water to air is dependent on water depth, chloroform transfer to air in water treatment unit processes would be much slower than in the experimental result

TABLE 11-1. CHLOROFORM CONCENTRATION AND POPULATION FOR 137 CITIES

City	NOMS, µg/l	NORS, µg/l	Average, µg/l	Population, 1980
Albuquerque, NM	ND	0.4	0.2	331,767
Amarillo, TX	7.6	--	7.6	149,230
Annandale, VA	79	67	73	49,524
Atlanta, GA	33	36	34.5	425,022
Baltimore, MD	41	32	36.5	786,775
Baton Rouge, LA	3	--	3	219,419
Billings, MT	4	--	4	66,798
Birmingham, AL	28	--	28	284,413
Bismark, ND	56	--	56	44,485
Boise, ID	8	--	8	102,451
Boston, MA	3.4	4	3.7	562,994
Brownsville, TX	10	12	11	84,997
Buffalo, NY	3.5^a	10	6.8	357,870
Burlington, VT	63	--	63	37,712
Camden, AR	12	40	26	15,356
Cape Girardeau, MO	31	116	73.5	34,361
Casper, WY	35	--	35	51,016
Cheyenne, WY	81	--	81	47,283
Charleston, SC	171	195	183	69,510
Charlotte, NC	36	--	36	314,447
Chattanooga, TN	37	30	33.5	169,565
Chicago, IL	14	15	14.5	3,005,072
Cincinnati, OH	--	45	45	385,457
Clarinda, IA	--	48	48	5,458
Cleveland, OH	12	18	15	573,822
Clinton, IL	--	4	4	8,014
Coalinga, CA	--	16	16	6,593
Columbus, OH	208	134	171	564,871
Concord, CA	16	31	23.5	103,255
Corvallis, OR	ND	26	13	40,960
Dallas, TX	18	18	18	904,078
Davenport, IA	63	88	75.5	103,264
Dayton, OH	4	8	6	203,371
Denver, CO	15	14	14.5	492,365
Des Moines, IA	ND	--	ND	191,003
Detroit, MI	9	12	10.5	1,203,339
Dos Palos, CA	--	61	61	3,123
Douglas, AK	--	40	40	19,528
Duluth, MN	7	--	7	92,811
Elizabeth, NJ	27	--	27	106,201
Erie, PA	18	--	18	119,123
Eugene, OR	19	--	19	105,624
Fort Wayne, IN	62	--	62	172,196
Fort Worth, TX	3	--	3	385,164
Fresno, CA	ND	--	ND	218,202
Grand Forks, ND	--	3	3	43,765
Grand Rapids, MI	48	--	48	181,843
Greenville, MS	ND	17	8.5	40,613
Hackensack, NJ	44	--	44	36,039
Hagerstown, MD	40	--	40	34,132
Hartford, CT	13	--	13	136,392
Hopewell, VA	--	6	6	23,397
Houma, LA	91	134	112.5	32,602
Houston, TX	123	--	123	1,595,138
Huntington, WV	7.2	23	15.1	63,684

CONTINUED

TABLE 11-1. (CONTINUED)

City	NOMS, µg/l	NORS, µg/l	Average, µg/l	Population, 1980
Huron, SD	193	309	251	13,000
Idaho Falls, ID	--	2	2	39,590
Illwaco, WA	174	167	169.5	604
Indianapolis, IN	36[b]	31	33.5	700,807
Jackson, MS	267	--	267	202,895
Jacksonville, FL	9	9	9	540,920
Jersey City, NJ	42	--	42	223,532
Kansas City, MO	29	24	26.5	448,159
Las Vegas, NV	22	--	22	164,674
Lawrence, MA	--	91	91	63,175
Lincoln, ND	5	4	4.5	656
Little Falls, NJ	64	59	61.5	11,496
Little Rock, AR	71[a]	--	71	158,461
Logansport, LA	--	28	28	1,565
Los Angeles, CA	32	32	32	2,966,850
Louisville, KY	67	--	67	298,451
Madison, WI	ND	--	ND	170,616
Manchester, NH	61	--	61	90,936
Melbourne, FL	271	--	271	46,536
Memphis, TN	4	0.9	2.5	646,356
Miami, FL	--	311	311	346,865
Milwaukee, WI	8.8	9	8.9	636,212
Monroe, LA	46	--	46	57,597
Montgomery, AL	55	--	55	177,857
Mount Clemons, MI	18	8.5[c]	11.7	18,806
Nashville, TN	8	16	12	455,651
Newark, DE	--	0.5	0.5	25,247
New Haven, CT	30	--	30	126,109
Newport, RI	74	103	88.5	29,259
New York, NY	--	22	22	7,071,639
Norfolk, VA	70	--	70	266,979
Oakland, CA	31	44	37.4	339,337
Oklahoma City, OK	200	--	200	403,213
Omaha, NB	42	--	42	314,255
Oshkosh, WI	--	26	26	49,620
Ottumwa, IA	--	0.9	0.9	27,381
Philadephia, PA	--	86	86	1,688,210
Phoenix, AZ	127	9	68	789,704
Piqua, OH	--	131	131	20,480
Pittsburgh, PA	19	8	13.5	423,938
Portland, ME	4.4	--	4.4	61,572
Portland, OR	7	--	7	366,383
Poughkeepsie, NY	50	--	50	29,757
Providence, RI	5	--	5	156,804
Provo, UT	19	--	19	74,108
Pueblo, CO	12	2	7	101,686
Rhinebeck, NY	--	8	8	2,542
Richmond, VA	17	--	17	219,214
Rockford, IL	ND	--	ND	139,712
Rome, GA	65	--	65	29,654
Sacramento, CA	5.6	--	5.6	275,741
Salt Lake City, UT	20	20	20	163,033
San Antonio, TX	ND	0.2	0.1	785,880
San Diego, CA	35	52	43.5	875,538
San Francisco, CA	76	41	58.5	678,974

CONTINUED

TABLE 11-1. (CONTINUED)

City	NOMS µg/l	NORS, µg/l	Average, µg/l	Population, 1980
San Juan, PR	--	47	47	--
Sante Fe, NM	60	--	60	48,953
Seattle, WA	--	15	15	493,846
Sioux Falls. SD	41	--	41	81,343
Spokane, WA	ND	--	ND	171,300
Springfield, MA	18	--	18	152,319
St. Croix, VI	62	--	62	--
St. Louis, MO	8.1	55	31.6	453,085
St. Paul, MN	8.6	--	8.6	270,230
Strasburg, PA	--	ND	ND	1,999
Syracuse, NY	8.6	--	8.6	170,105
Tacoma, WA	1.5	--	1.5	158,501
Tampa, FL	109	--	109	271,523
Toledo, OH	20	--	20	354,635
Toms River, NJ	--	0.6	0.6	7,465
Topeka, KS	118	88	103	115,266
Tucson, AZ	--	0.2	0.2	330,537
Tulsa, OK	20	--	20	360,919
Washington, DC	53	41	47	638,333
Waterbury, CT	77	93	85	103,266
Waterford Township, NY	48	--	48	2,405
Wheeling, WV	70	72	71	43,070
Whiting, IN	1.2[a]	--	1.2	5,630
Wichita, KS	6.1	0.5	3.3	279,272
Wilmington-Stanton, DE	18	23	20.5	75,690
Youngstown, OH	--	80	80	115,436
Yuma, AZ	27	--	27	42,433

[a] Phase II sample.

[b] Phase III sample.

[c] Average of 2 samples.

cited above. Consumer uses other than drinking, such as washing, watering, cooking, bathing, and industrial processes, subjects water to conditions such as aeration, agitation, boiling, stirring, sprinkling, and periods of quiescence that, according to results of experiments, promote chloroform evaporation.[8,9]

As shown by Figure 11-2, chloroform is formed over a period of time from the reaction of chlorine with organic precursors in the water. Hence, the chloroform formation potential of chlorinated water is not reached for several days after chlorine addition. Because typical water treatment takes less than 10 hours (from alum mix to final disinfection), in many cases the majority of chloroform in tap water will form in the distribution system after treatment. Considering the chloroform water-to-air transfer rate and the time-dependence of the chloroform formation reaction, the potential for chloroform air emissions is greatest after water leaves the treatment plant. Most chloroform air emissions from drinking water, therefore, probably result from consumer use of water in the area served by the distribution system.

Chloroform Emissions Estimates

National Emissions Estimates--

The chloroform concentrations from different U.S. cities shown in Table 11-1 indicate that the chloroform formation potential of source waters varies widely across the country. Chloroform produced in drinking water can be estimated by averaging the concentrations measured in the NORS and NOMS, then multiplying the average chloroform concentration by the quantity of water chlorinated in the U.S. annually. The volume of water treated in each city was estimated by multiplying the population by the estimated water consumption of 587 liters per capita per day (155 gallons per capita per day).[10] If a city was sampled in both NORS and NOMS, the data were averaged. The amount of chloroform generated in each of the 137 cities sampled was divided by the total amount of water treated to give a weighted average of 41 μg/l of chloroform. The national quantity of water chlorinated was estimated by multiplying the population served by primary water supplies (214,000,000) by the estimated per capita consumption, yielding an estimated 4.6×10^{13} liters per year chlorinated drinking water. Multiplying the

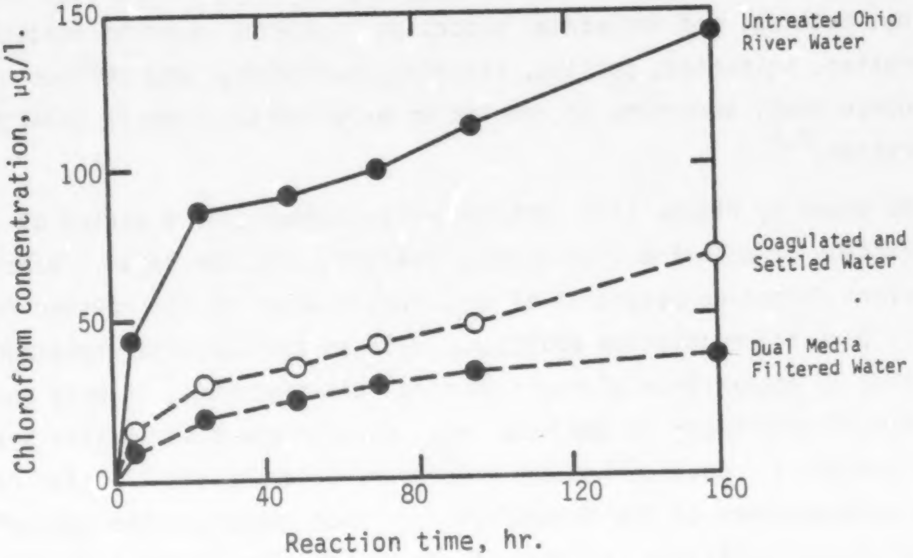


Figure 11-2. Chloroform formation potential in raw and treated water.[11]

national average chloroform concentration of 41 μg/l by the national quantity of chlorinated drinking water yields 1,900 Mg/yr chloroform produced from chlorination. Discounting the relatively small amount of tap water ingested, almost all of the chloroform produced evaporates to the atmosphere.

Model Plant Emissions Estimates--

The Office of Drinking Water has developed six different-sized model water treatment plants for the purpose of estimating chloroform control costs. These model plants were developed to cover the range of treatment plant sizes serving greater than 10,000 people. Treatment plant capacities, average water production, and the estimated average population served by each system size are presented in Table 11-2. The model plants were used to estimate the quantity of chloroform produced annually in different-sized treatment plants at various concentration levels. The quantities are presented for a range of concentrations because chloroform formation varies considerably between U.S. water treatment plants. The annual chloroform produced from chlorination in each system size at concentrations between 10 μg/l and 100 μg/l is presented in Table 11-3. The quantities produced range from 36.5 kg/yr to 35,478 kg/yr.

CHLOROFORM CONTROL METHODS

Chloroform in drinking water is presently regulated by the National Interim Primary Drinking Water Regulations; Trihalomethanes (40 CFR Part 142). The rule establishes a maximum total trihalomethane (TTHM) contaminant level of 0.10 mg/l for all public water systems serving more than 10,000 persons and specifies what treatment methods a system may be required to install or use to comply with the TTHM MCL. While trihalomethanes in drinking water also include bromoform, dibromochloromethane, and bromodichloromethane, chloroform is the predominant species.

The TTHM rule identifies two categories of control methods: (1) those technologies or treatment techniques determined to be "generally available", taking costs into consideration; and (2) those technologies or treatment techniques not determined to be "generally available", but which may be available to some systems. The control methods identified in the TTHM rule are presented below as potential chloroform controls.

TABLE 11-2. MODEL WATER PLANTS AND AVERAGE POPULATION SERVED[12]

Plant capacity, 10^6 l/d	Average water production, 10^6 l/d	Average population served[a]
16	10	17,035
35	22	37,480
69	43	73,254
102	64	109,029
286	190	323,680
1,362	972	1,655,877

[a] Based on average per capita consumption of 587 liters/day.

TABLE 11-3. ANNUAL CHLOROFORM PRODUCTION IN MODEL PLANTS AT VARIOUS CONCENTRATIONS

System average water production, 10^6 l/d	Annual chloroform production at given concentration (kg)			
	10 μg/l	20 μg/l	50 μg/l	100 μg/l
10	36.5	73	182.5	365
22	80.3	160.6	401.5	803
43	157	314	784.8	1,569.6
64	233.6	467.2	1,168	2,336
190	693.5	1,387	3,467.5	6,935
972	3,547.8	7,095.6	17,739	35,478

Effective control techniques for limiting chloroform in drinking water follow three approaches: precursor removal prior to chlorination; chloroform removal following chlorination; and use of a disinfectant that does not react with precursors to form chloroform.

EPA has identified the best technologies, treatment techniques and other means generally available, taking costs into consideration, that can be used by community water systems for controlling total trihalomethanes, including chloroform.[13] The five techniques listed by EPA as being "generally available" (also called Group I techniques) are: use of chloramines as an alternate or supplemental disinfectant or oxidant; use of chlorine dioxide as an alternate or supplemental disinfectant or oxidant; improving existing clarification for precursor removal; moving the point of chlorination to reduce chloroform formation and, where necessary, replacing chlorine used as a pre-oxidant with chloramines, chlorine dioxide, or potassium permanganate; and the use of powdered activated carbon (PAC) for chloroform precursor or chloroform reduction seasonally or intermittently at dosages not to exceed 10 mg/l on an average annual basis.

In addition, EPA has identified five other methods not considered "generally available" (also called Group II methods) that must be studied for technical and economic feasibility for TTHM reduction in the event Group I methods are not effective in reducing TTHMs sufficiently in a particular water system. These five Group II methods are: introduction of off-line water storage; aeration for reduction of chloroform; introduction of clarification; consideration of alternate sources of raw water; and use of ozone as an alternate or supplemental disinfectant or oxidant.[13] Of these, only aeration does not reduce chloroform production; rather, aeration transfers chloroform from water to air. Thus, aeration is not an air emissions control technique.

Generally Available Control Methods

Use of Chloramines--

Chloramines, which have been widely used for many years in the United States as a drinking water disinfectant, do not react with organic precursor material to form chloroform.[14] Several cities in the U.S. have already reduced chloroform in drinking water by using chloramines.[15,16] Chloramines are produced in treatment plant water from the reaction of free chlorine and ammonia. In chlorine-ammonia treatment for primary disinfection, chlorine and ammonia are added to the water simultaneously or in succession typically at a 4:1 chlorine to ammonia ratio. Although the reaction to form chloramines occurs in hundredths of a second at high temperatures and optimum pH (8.3), it proceeds at much slower rates at lower temperatures and other pH values.[17] If ammonia addition is delayed, or if the reaction between free chlorine and ammonia proceeds slowly, free chlorine could be present for several minutes or even several hours.

Several cities have reduced chloroform concentrations by using chloramines. The Louisville Water Company reduced the total trihalomethane (mostly chloroform) concentration by adding ammonia to drinking water 10 minutes after adding chlorine. The trihalomethane concentration was reduced from 150 μg/l to 15 μg/l.[15]

Breakpoint chlorination, the practice of adding chlorine until all natural nitrogen compounds in the water have formed combined chlorine, was replaced by chlorine and ammonia addition following lime softening at a treatment plant in Miami, Florida. As a result, the chloroform concentration in finished water decreased from an average of over 100 μg/l to an average of approximately 10 μg/l.[16] Moreover, the persistence of the chloramine residual has eliminated the need for chlorine booster stations.

As shown by these utilities, the use of chloramines can significantly reduce chloroform levels in treated water. Reductions of 90 percent and controlled chloroform concentrations of 10 μg/l are possible.

Use of Chlorine Dioxide --

Laboratory studies and use in water treatment plants show that chlorine dioxide will disinfect without forming chloroform. Several plants in the United States presently use chlorine dioxide for taste and odor control, disinfection, oxidation of organics, and removal of iron, manganese and color.[18] Chlorine dioxide is an excellent biocide with an ability to inactivate bacteria and viruses at a rate close to that of free chlorine.

Chlorine dioxide equipment can be retrofitted into water treatment plants. Existing chlorination equipment can be used as standby. Because chlorine dioxide is unstable, it must be generated and used on-site. Reactor vessels are available from U.S. manufacturers, but the simplicity of design has encouraged several plants to fabricate their own.[18] Small amounts of chlorine are carried over in chlorine dioxide production and form free chlorine in the water. However, a study has shown that even when the free chlorine concentration is half that of chlorine dioxide, chloroform formation is reduced by 90 percent.[19]

Improved Existing Clarification --

Improved clarification can often lower chloroform concentrations in treated water by removing a larger fraction of organic precursor material. In conventional clarification, coagulants such as iron salts and aluminum sulfate (alum), calcium hydroxide (if softening is also a goal), and polymers are used in different types of water treatment plants to remove color and turbidity from raw water.[20] A typical clarification process involves coagulant addition and mixing, flocculation, and sedimentation. While coagulation is most often considered a treatment technique for turbidity reduction, the process plays an important part in removing organics, including chloroform precursors such as humic and fulvic acids. This role occurs both because some organic materials are absorbed on suspended particles (turbidity) and because direct interactions of the natural humic materials (usually recognized as color) take place with the coagulants themselves.[20] The American Water Works Association Research Committee on Coagulation has concluded that both iron salts and alum are effective in removing humic and fulvic acids from water, and that cationic polymers that interact with anionic humates can be useful as coagulants for organics removal.[21] Thus, improved clarification could be expected to lower chloroform concentrations in treated water by removing a larger fraction of chloroform precursors.

Because the organic content of raw water can vary greatly between sources, any change in coagulant dose or type or in water pH for the purpose of improving clarification precursor removal should be tested for source-specific removal efficiency. The degree of improvement in clarification possible in a treatment plant depends on the level of treatment already practiced in the clarification process. Some water treatment plants may already be operating the coagulation-sedimentation process near a level of maximum organics removal while others may not.[22]

Moving the Point of Chlorination--

Moving the chlorination point in a treatment plant to control chloroform is a technique closely associated with clarification. This technique is applicable to water treatment plants that chlorinate raw water (prechlorination) or gravity-settled water before it is treated with coagulant and clarified by sedimentation. As described above, raw water often contains certain amounts of organic chloroform precursor materials that can be removed by gravity settling or coagulation and sedimentation. If chlorine is added before gravity settling or coagulation and sedimentation, it reacts with the precursors to form chloroform before the precursors can be removed. Because gravity settling and coagulation-sedimentation take a relatively large amount of time (compared to other water treatment unit processes), prechlorination allows considerable time for chloroform formation.[23] Thus, in many cases, moving chlorination to a point after coagulation and sedimentation reduces the amount of precursor material that the chlorine can react with, and consequently reduces the amounts of chloroform produced in the water.

Moving the chlorination point has been ineffective in reducing chloroform in some water treatment plants and quite effective in others (assumed from a reduction of total trihalomethanes). The potential effectiveness of moving the chlorination point can be determined by measuring the removal of precursors at different points in the treatment train. This technique best reduces chloroform concentrations if a high percentage of chloroform precursors are settled out during clarification.

Use of Powdered Activated Carbon--

Powdered activated carbon (PAC) can be used to remove both chloroform and chloroform precursors from water through adsorption.[24] According to one study on Ohio River water, about 77 mg/l PAC is needed to lower chloroform formation potential from 200 μg/l to 100 μg/l.[25] Because the use of such high dosages is likely to cause sludge problems as well as be prohibitively expensive, the TTHM drinking water rule recommends limiting PAC use to an annual average of 10 mg/l.[13] In some treatment plants where high chloroform concentrations are experienced seasonally, intermittent high dosages of PAC may sufficiently reduce peak chloroform levels without exceeding the 10 mg/l annual average.

Additional Control Methods Not Considered Generally Available

In addition to the five Group I control methods described above as "generally available", EPA has identified five Group II control methods that must be considered in the event that none of the Group I control techniques reduces trihalomethane concentrations sufficiently. The five Group II methods are described briefly below.

Off-Line Water Storage--

Off-line water storage in a reservoir before coagulation, flocculation, and sedimentation has been practiced by some utilities for many years. The purpose of this treatment is to provide an extended period of time for solids to settle out, thereby reducing the load on the treatment process, mitigating extreme changes in water quality from stormwater runoff, and providing a source of water during intermittent pollution episodes.[26]

Aeration for Chloroform Removal--

Aeration has long been used in drinking water treatment to reduce taste and odors, remove carbon dioxide, and oxidize iron and manganese for subsequent removal. While aeration may be appropriate and effective for controlling chloroform as a drinking water contaminant in some situations, it is not an air emissions control technique.

Introduction of Clarification--

Many treatment plants currently treat their water without sedimentation or filtration. The addition of either of these clarification processes might remove a substantial fraction of chloroform precursors, and would also contribute to the removal of pathogens and to more effective disinfection.

Alternate Source of Raw Water--

Some utilities may have access to other sources of raw water that are low in precursor concentrations. The use of a new water source may result in overall water treatment savings as well as a reduction in chloroform levels.

The technical and economic feasibility of an alternate water source must be determined for each site. Costs for changing source water can be quite high and vary widely.

Use of Ozone--

Ozone can be used in water treatment as an alternate or supplemental disinfectant or oxidant. Ozone is an efficient disinfectant that does not form chloroform. It is widely used for disinfection in Europe, Canada, and the Soviet Union.[27] Communities in the United States which have added ozone to their water treatment have had little difficulty in obtaining the necessary guidance, equipment, and service help.[28] Pilot-scale ozonation systems and maintenance service contracts can be obtained from manufacturers.

The disadvantages of ozone are its higher cost than chlorine, lack of sufficient residual protection, and its potential for forming organic byproducts with unknown health risks.[29]

A typical ozone installation utilizes a dosage of 3 mg/l with a detention time of 10 minutes, from an ozone generator with a capacity to produce 4.5 mg/l.

CHLOROFORM CONTROL COSTS

The estimated costs of applying Group I chloroform control methods to different sizes of water treatment plants are discussed and presented below. Capital costs, operating costs, and design criteria are presented for each Group I chloroform control method applied to the six model treatment plant sizes presented in Table 11-3.

Use of Chloramines

For the purpose of estimating costs, the design criteria for using chloramines are: addition of ammonia to chlorinated water at a 4:1 chlorine to ammonia ratio to produce chloramines; an average combined chlorine residual of 3 mg/l; use of existing chlorine feed equipment and addition to ammonia feed and storage equipment; and use of either aqueous or anhydrous ammonia.[30] The total annualized costs for this method, presented in Table 11-4, range from $8,000 for the smallest system to $99,000 for the largest system.

Use of Chlorine Dioxide

The design criteria for estimating the costs of using chlorine dioxide are: chlorine dioxide at a dose of 1 mg/l would replace chlorine as the disinfectant; a reaction vessel would be used to combine one part chlorine with one part sodium chlorite; and existing chlorination equipment would be

TABLE 11-4. TOTAL ANNUALIZED COST OF CONTROLLING CHLOROFORM BY USING CHLORAMINES[31]

Plant capacity, 10^6 l/day	Average water production, 10^6 l/day	Average capital cost, $1,000	Annualized capital cost, $1,000[a]	Average annual operating cost, $1,000	Average total annualized cost, $1,000
16	10	28	3	5	8
35	22	36	4	7	11
69	43	60	7	13	20
102	64	70	8	17	25
286	190	99	12	40	51
1,362	972	208	25	175	99

[a] Based on a 20-year life and 10 percent interest.

modified to feed smaller amounts of chlorine, saving 1.5 mg of chlorine per liter.[32] The capital and operating costs for using chlorine dioxide are presented in Table 11-5. The total annualized costs range from $22,000 for the smallest plant to $997,000 for the largest plant.

Use of Improved clarification

The costs for improving clarification are based on increasing the alum dosage by 10 mg/l; installing a polymer feed system which will add polymer at the rate of 0.5 mg/l; and improving the inlet baffling.[32] The total annualized costs, presented in Table 11-6, range from $17,000 for the smallest system to $1.12 million for the largest system.

Modifying Chlorination

The costs for modifying chlorination are based on the assumptions that chlorine will be added to a point following sedimentation and that an alternate oxidant will replace chlorine (used in prechlorination). The possible alternate oxidants are potassium permanganate (at a dosage of 0.5 mg/l), hydrogen peroxide (at 2.0 mg/l), chlorine dioxide (at 0.5 mg/l), and chloramines (at 2.0 mg/l). The average annualized costs presented in Table 11-7 are based on replacing chlorine with potassium permanganate (the least cost by replacement chemical).[33] The annualized costs are $7,000 for the smallest size category and $317,000 for the largest category.

Use of Powdered Activated Carbon

The costs for using PAC are based on the following criteria: all PAC storage and feed equipment exists on site; the average annual PAC dosage is 7.5 mg/l; the use of PAC results in additional sludge disposal costs; and PAC is delivered in bulk quantities.[34] The annual cost of using PAC is proportional to the quantity used and is presented in Table 11-8. The annual cost for the smallest size category is $32,000, and for the largest size category $3.09 million.

CHLOROFORM CONTROL COST-EFFECTIVENESS

The cost-effectiveness of reducing potential chloroform air emissions from chlorinated municipal drinking water is the ratio of the cost of applying a control method in a treatment plant to the resulting reduction in chloroform emissions. For this analysis, all reductions in chloroform

TABLE 11-5. TOTAL ANNUALIZED COST OF CONTROLLING CHLOROFORM BY USING CHLORINE DIOXIDE[35]

Plant capacity, 10^6 l/day	Average water production, 10^6 l/day	Average capital cost, \$1,000	Annualized capital cost, \$1,000[a]	Average annual operating cost, \$1,000	Average total annualized cost, \$1,000
16	10	47	6	16	22
35	22	55	6	29	35
69	43	63	7	54	61
102	64	120	14	73	87
286	190	174	20	201	221
1,362	972	420	49	948	997

[a] Based on a 20-year life and 10 percent interest (capital recovery factor = 0.1175).

TABLE 11-6. TOTAL ANNUALIZED COST OF CONTROLLING CHLOROFORM BY IMPROVING CLARIFICATION[36]

Plant capacity, 10^6 l/day	Average water production, 10^6 l/day	Average capital cost, \$1,000	Annualized capital cost, \$1,000[a]	Average annual operating cost, \$1,000	Average total annualized cost, \$1,000
16	10	34	4	13	17
35	22	46	5	25	30
69	43	70	8	49	57
102	64	92	11	71	82
286	190	198	23	208	231
1,362	972	626	74	1,046	1,120

[a] Based on a 20-year life and 10 percent interest.

TABLE 11-7. TOTAL ANNUALIZED COST OF CONTROLLING CHLOROFORM BY MODIFYING CHLORINATION[37]

Plant capacity, 10^6 l/day	Average water production, 10^6 l/day	Average capital cost, $1,000	Annualized capital cost, $1,000[a]	Average annual operating cost, $1,000	Average total annual cost, $1,000
16	10	15	2	5	7
35	22	16	2	10	12
69	43	20	2	17	19
102	64	25	3	23	26
286	190	29	3	62	65
1,362	972	52	6	311	317

[a] Based on a 20-year life and 10 percent interest.

TABLE 11-8. TOTAL ANNUALIZED COST OF CONTROLLING CHLOROFORM BY USING POWDERED ACTIVATED CARBON[34]

Plant capacity, 10^6 l/day	Average water production, 10^6 l/day	Average capital cost, $1,000	Annualized capital cost, $1,000	Average annual operating cost, $1,000	Average total annual cost, $1,000
16	10	0	0	32	32
35	22	0	0	70	70
69	43	0	0	137	137
102	64	0	0	203	203
286	190	0	0	606	606
1,362	972	0	0	3,093	3,093

formation in treated water were considered reductions in air emissions. The cost-effectiveness of the Group I control methods described above are presented below. The reductions achievable by these control techniques vary from plant to plant, and depend on the quality of water and treatment processes in place. The rate of chloroform formation, the chloroform formation potential, and the effectiveness of any chloroform reduction technique are dependent upon type and quantity of precursors present as well as parameters such as pH and temperature. Thus, there is no general one-to-one correspondence between control technique and level of control achieved.

Because the results of any given control method have been shown to vary considerably between treatment plants, no typical control efficiency can be ascribed to a particular control method. Hence, the cost-effectiveness of a control method cannot be estimated based on an assumed control efficiency. Cost-effectiveness can, however, be estimated based on the amount of chloroform "controlled". This amount, in turn, can be calculated from the reduction in chloroform concentration in treated water resulting from applying a control method. As shown in Table 11-3, for example, the quantity of chloroform produced annually in the smallest model plant increases or decreases by 36.5 kg for each 10 µg/l increase or decrease in chloroform concentration, regardless of the initial concentration. Because the cost of a control method for a specific plant size is constant, the cost-effectiveness of control depends on the quantity of chloroform controlled (or, in other words, on the decrease in chloroform concentration in treated water resulting from control). The cost-effectiveness of each control method is presented in Tables 11-9 through 11-13 for concentration reductions ranging from 10 µg/l to 100 µg/l. Using these tables, the cost-effectiveness of a particular control method can be estimated for a plant for varying amounts of control. The cost-effectiveness is the same for a given increment of concentration reduction in a plant, whatever the initial concentration. For example, in the smallest model plant (10 million l/d average production) the cost-effectiveness of using chloramines (Table 11-9) will be $110,000/Mg for a 20 µg/l decrease in the chloroform concentration whether the concentration was reduced from 120 µg/l to 100 µg/l or from 25 µg/l to 5 µg/l.

TABLE 11-9. ESTIMATED TOTAL ANNUAL COST AND COST-EFFECTIVENESS OF CONTROLLING CHLOROFORM IN DRINKING WATER BY USING CHLORAMINES

Plant capacity 10^6 ℓ/d	Average production 10^6 ℓ/d	Average capital cost $1000	Annualized capital cost $1000[a]	Average annual operating cost, $1000	Average total annual cost, $1000	Cost-effectiveness, $1000/Mg chloroform[b]					
						Concentration reduced by 10 μg/ℓ	Concentration reduced by 20 μg/ℓ	Concentration reduced by 30 μg/ℓ	Concentration reduced by 40 μg/ℓ	Concentration reduced by 50 μg/ℓ	Concentration reduced by 100 μg/ℓ
16	10	28	3	5	8	219	110	72.7	54.8	43.7	21.9
35	22	36	4	7	11	137	68	45.6	34.3	27.4	13.7
69	43	60	7	13	20	127	63.7	42.5	31.8	25.5	12.7
102	64	70	8	17	25	107	53.5	35.7	26.8	21.4	10.7
286	190	99	12	40	51	73.5	36.7	24.5	18.4	14.7	7.3
1,362	972	208	25	175	99	27.9	13.9	9.3	7.0	5.6	2.8

[a] Based on 20 year life and ten percent interest (capital recovery factor = 0.1175).

[b] Based on average total annual cost, average water production, and emission reduction.

TABLE 11-10. ESTIMATED TOTAL ANNUAL COST AND COST-EFFECTIVENESS OF CONTROLLING CHLOROFORM IN DRINKING WATER BY USING CHLORINE DIOXIDE

Plant capacity 10^6 ℓ/d	Average production 10^6 ℓ/d	Average capital cost $1000	Annualized capital cost $1000[a]	Average annual operating cost, $1000	Average total annual cost, $1000	Cost-effectiveness, $1000/Mg chloroform[b]					
						Concentration reduced by 10 μg/ℓ	Concentration reduced by 20 μg/ℓ	Concentration reduced by 30 μg/ℓ	Concentration reduced by 40 μg/ℓ	Concentration reduced by 50 μg/ℓ	Concentration reduced by 100 μg/ℓ
16	10	47	6	16	22	603	301	200	151	120	60.3
35	22	55	6	29	35	436	217	145	109	87.1	43.6
69	43	63	7	54	61	389	194	130	97.1	77.7	38.9
102	64	120	14	73	87	372	186	124	93.1	74.4	37.2
286	190	174	20	201	221	319	159	106	79.8	63.7	31.9
1,362	972	420	49	948	997	281	140	94.0	70.2	56.3	28.1

[a] Based on 20 year life and ten percent interest (capital recovery factor = 0.1175).

[b] Based on average total annual cost, average water production, and emission reduction.

TABLE 11-11. ESTIMATED TOTAL ANNUAL COST AND COST-EFFECTIVENESS OF CONTROLLING CHLOROFORM IN DRINKING WATER BY IMPROVING CLARIFICATION

Plant capacity 10^6ℓ/d	Average production 10^6ℓ/d	Average capital cost \$1000[a]	Annualized capital cost \$1000[b]	Average annual operating cost, \$1000	Average total annual cost, \$1000	Cost-effectiveness, \$1000/Mg chloroform[c]					
						Concentration reduced by 10μg/ℓ	Concentration reduced by 20μg/ℓ	Concentration reduced by 30μg/ℓ	Concentration reduced by 40μg/ℓ	Concentration reduced by 50μg/ℓ	Concentration reduced by 100μg/ℓ
16	10	34	4	13	17	466	233	155	116	92.9	46.6
35	22	46	5	25	30	373	186	124	93.5	74.6	37.3
69	43	70	8	49	57	363	182	121	90.8	72.6	36.3
102	64	92	11	71	82	351	176	117	87.8	70.1	35.1
286	190	198	23	208	231	333	166	111	83.4	66.6	33.3
1,362	972	626	74	1,046	1,120	316	158	106	78.9	63.3	31.6

[a] Capital costs for 5 percent of the systems could be as much as 20 times higher than the average cost.

[b] Based on 20 year life and ten percent interest (capital recovery factor = 0.1175).

[c] Based on average total annual cost, average water production, and emission reduction.

TABLE 11-12. ESTIMATED TOTAL ANNUAL COST AND COST-EFFECTIVENESS OF CONTROLLING CHLOROFORM IN DRINKING WATER BY MODIFYING CHLORINATION

Plant capacity 10^6ℓ/d	Average production 10^6ℓ/d	Average capital cost \$1000	Annualized capital cost \$1000[a]	Average annual operating cost, \$1000	Average total annual cost, \$1000	Cost-effectiveness, \$1000/Mg chloroform[b]					
						Concentration reduced by 10μg/ℓ	Concentration reduced by 20μg/ℓ	Concentration reduced by 30μg/ℓ	Concentration reduced by 40μg/ℓ	Concentration reduced by 50μg/ℓ	Concentration reduced by 100μg/ℓ
16	10	15	2	5	7	192	95.9	63.6	47.9	38.3	19.2
35	22	16	2	10	12	149	74.5	49.8	37.4	29.9	14.9
69	43	20	2	17	19	121	60.5	40.3	30.3	24.2	12.1
102	64	25	3	23	26	111	55.7	37.1	27.8	22.2	11.1
286	190	29	3	62	65	93.7	46.8	31.3	23.5	18.7	9.37
1,362	972	52	6	311	317	89.4	44.6	29.9	22.3	17.9	8.94

[a] Based on 20 year life and ten percent interest (capital recovery factor = 0.1175).

[b] Based on average total annual cost, average water production, and emission reduction.

TABLE 11-13. ESTIMATED TOTAL ANNUAL COST AND COST-EFFECTIVENESS OF CONTROLLING CHLOROFORM IN DRINKING WATER BY USING POWDERED ACTIVATED CARBON

Plant capacity 10^6ℓ/d	Average production 10^6ℓ/d	Average capital cost $1000	Annualized capital cost $1000[a]	Average annual operating cost, $1000	Average total annual cost, $1000	Cost-effectiveness, $1000/Mg chloroform[b]					
						Concentration reduced by 10μg/ℓ	Concentration reduced by 20μg/ℓ	Concentration reduced by 30μg/ℓ	Concentration reduced by 40μg/ℓ	Concentration reduced by 50μg/ℓ	Concentration reduced by 100μg/ℓ
16	10	0	0	32	32	877	438	291	219	175	87.7
35	22	0	0	70	70	872	437	290	218	174	87.2
69	43	0	0	137	137	873	436	291	218	175	87.3
102	64	0	0	203	203	869	435	290	217	174	86.9
286	190	0	0	606	606	874	436	291	219	175	87.4
1,362	972	0	0	3,093	3,093	871	436	292	218	175	87.1

[a] Based on 20 year life and ten percent interest (capital recovery factor = 0.1175).

[b] Based on average total annual cost, average water production, and emission reduction.

CONCLUSIONS

While the amount of chloroform present in drinking water generally is small, it will evaporate from water during consumer use, exposing consumers to chloroform air emissions. The trihalomethane drinking water standard requires the TTHM concentration to be less than 0.10 mg/l, a standard that most community water supplies have complied with. The Office of State Programs receives from the States only reports of violations of the MCL by water treatment systems and therefore has no information on how many systems have had to implement control measures.[38] The cost-effectiveness of the Group I control techniques presently used is variable, but based on reasonable assumptions is shown to range from $2,800/Mg to $877,000/Mg (Tables 11-9 through 11-13). Any reduction in chloroform concentration beyond the present levels in treatment plants may require control techniques not considered generally available by the Office of Drinking Water. These treatment techniques certainly would cost more than the Group I techniques discussed above, and may not be applicable to every plant.

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12. MUNICIPAL WASTEWATER TREATMENT

Chloroform is formed in municipal wastewater by the reaction of organic compounds in wastewater with chlorine containing compounds entering the sewerage system (such as sodium hypochlorite or bleach), or by the reaction of organic compounds in the effluent with chlorine used for disinfection. Tests by EPA's Effluent Guidelines Division on 50 POTW's showed that on average chloroform concentrations in wastewater dropped 4.6 μg/l, from 15 μg/l in the influent to 10.4 μg/l in the secondary effluent. Tests by EPA's Effluent Guidelines Division on secondary effluent indicate that the average chloroform concentration in municipal wastewater increases 8 μg/l following chlorine disinfection.[1]

In 1982, 8,480 Publicly Owned Treatment Works (POTW's) chlorinated effluent for disinfection, with a combined flow of 92,081,000 cubic meters per day (24,325 mgd).[2] Applying the 4.6 μg/l factor to the amount of wastewater treated, 154.6 Mg/yr of chloroform are emitted from POTW's. Applying the 8 μg/l factor to the amount of wastewater disinfected annually, 268.9 Mg of chloroform is generated per year following wastewater treatment.

Although all of the chloroform is originally in water, tests indicate that the majority of chloroform generated ends up in the air. Volatilization from water depends on the solubility, vapor pressure and molecular weight of the pollutant and physical properties (e.g. flow velocity, depth, and turbulence) of the water body and atmosphere above it. Chloroform has a vapor pressure (P_{vp}) of 0.32 atm at 20°C and a water solubility (S) of 67 mol/m^3. Thus, Henry's law constant (P_{vp}/S) is calculated to be 4.8×10^{-3} atm-m^3/mol. When Henry's law constant is $>10^{-3}$ atm-m^3/mol, volatilization is rapid and the resistance of the water film dominates volatilization.

CONTROL TECHNIQUES, COSTS, AND COST-EFFECTIVENESS

Control techniques discussed below apply to controlling chloroform formation during disinfection. Control techniques for limiting chloroform formation include precursor removal prior to chlorination, and use of a disinfectant that does not react with precursors to form chloroform. A third option, chloroform removal following chlorination, would not be viable because this method removes chloroform from water by aeration thus hastening the intermedia transfer to air.

Precursor Removal

Although precursor removal prior to chlorination is possible, the practice of improved clarification to remove precursors is not practiced by POTW's. Improved clarification would require addition of coagulants such as iron salts and aluminum sulfate (alum) during the clarification stage. Addition of coagulants would increase flocculation and settling of total suspended solids. This would reduce the amount of precursors because some organic material is adsorbed on suspended particles.

Best demonstrated efficiency by use of improved clarification at water treatment plants indicates that improved clarification offers 37 percent removal efficiency.[3] Thus, on average, chloroform formation in treated wastewater could be reduced from 8 to 5 µg/l.

Control costs for improving clarification are based on using alum at a dosage of 10 mg/l; installing a polymer feed system which adds polymer at a rate of 0.5 mg/l; and improving inlet baffling.[4] These costs were derived for drinking water treatment systems and applied to POTW's. The total annualized costs, presented in Table 12-1, range from $17,000 for the smallest system to $1.12 million for the largest system.

The cost-effectiveness of installing improved clarification would range from $1.56 million per Mg for the smallest facility to $1.05 million per Mg for the largest facility (Figure 12-1). Reductions in chloroform formation potential, costs, and cost-effectiveness are shown in Table 12-2.

Chlorine Substitution

Chloramines--

Use of chloramines as a drinking water disinfectant has been used in the United States for many years and could also be used as a substitute for chlorine at wastewater treatment facilities. Chloramines, unlike chlorine, do not react with precursor material to form chloroform. Chloramines are produced in treatment plant water from the reaction of free chlorine and ammonia. When chlorine is added to water, two reactions take place to form free chlorine species. The hydrolysis reaction is

TABLE 12-1. TOTAL ANNUALIZED COST OF CONTROLLING CHLOROFORM BY IMPROVING CLARIFICATION

Plant capacity, 10^6 l/day	Average water production, 10^6 l/day	Average capital cost, $1,000	Annualized capital cost, $1,000[a]	Average annual operating cost, $1,000	Average total annualized cost, $1,000
16	10	34	4	13	17
35	22	46	5	25	30
69	43	70	8	49	57
102	64	92	11	71	82
286	190	198	23	208	231
1,362	972	626	74	1,046	1,120

[a] Based on a 20-year life and 10 percent interest.

TABLE 12-2. CHLOROFORM REDUCTION POTENTIAL, COSTS, AND COST-EFFECTIVENESS OF IMPROVED CLARIFICATION

Average amount of water treated, 10^6 l/day	Average $CHCl_3$ produced prior to improved clarification, Mg/yr[a]	Average $CHCl_3$ produced after improved clarification, Mg/yr[b]	$CHCl_3$ reduction potential, Mg/yr	Total annualized costs, $1,000	Cost-effectiveness $\$10^6$/Mg
10	2.9×10^{-2}	1.83×10^{-2}	1.09×10^{-2}	17	1.56
22	6.42×10^{-2}	4.02×10^{-2}	2.4×10^{-2}	30	1.25
43	1.25×10^{-1}	7.85×10^{-2}	4.65×10^{-2}	57	1.23
64	1.87×10^{-1}	1.17×10^{-1}	7.0×10^{-2}	82	1.17
190	5.55×10^{-1}	3.47×10^{-1}	2.08×10^{-1}	231	1.11
972	2.84×10^{0}	1.77×10^{0}	1.07×10^{0}	1,120	1.05

[a] Based on an average $CHCl_3$ increase of 8 μg/l

[b] Based on an average $CHCl_3$ increase of 5 μg/l

$$Cl_2 + H_2O \rightleftharpoons HOCl + Cl^- + H^+.$$

The ionization reaction is

$$HOCl \rightleftharpoons OCl^- + H^+.$$

When ammonia is added to the water the following reaction takes place to form monochloramine:

$$HOCl + NH_3 \rightleftharpoons NH_2Cl + H_2O.$$

In chlorine-ammonia treatment for primary disinfection, chlorine and ammonia are added to the water simultaneously or in succession typically at a 4:1 chlorine to ammonia ratio. Although the reaction to form chloramines occurs in hundredths of a second at high temperatures and optimum pH (8.3), it proceeds at much slower rates at lower temperatures and other pH values.[5] If ammonia addition is delayed, or if the reaction between free chlorine and ammonia proceeds slowly, free chlorine could be present for several minutes or even several hours.

The ionization reaction described above is highly influenced by pH, with hypochlorous acid (HOCl) the dominant species at low pH and hypochlorite ion (OCl^-) dominant at high pH values. The chloramine species present are also influenced by pH. The reaction equation

$$H^+ + 2NH_2Cl \rightleftharpoons NH_4 + NHCL_2$$

indicates that although mostly monochloramine is formed when excess ammonia is present at high pH (>8), lowering the pH will cause formation of dichloramine with the position of this equilibrium determined by the pH.[6] Thus, the pH determines the relative quantities of species present.

It has been estimated that use of chloramines can reduce chloroform formation by 90 percent. Thus, on average, chloroform formation in treated wastewater would be reduced from 8 to 0.8 μg/l.

For the purpose of estimating costs, the design criteria for using chloramines are: addition of ammonia to chlorinated water at a 4:1 chlorine to ammonia ratio to produce chloramines; an average combined chlorine residual of 3 μg/l; use of existing chlorine feed equipment and addition of ammonia feed and storage equipment; and use of either aqueous or anhydrous ammonia.[7] The total annualized costs for this method, presented in Table 12-3, range from $8,000 for the smallest system to $99,000 for the largest system.

TABLE 12-3. TOTAL ANNUALIZED COST OF CONTROLLING CHLOROFORM BY USING CHLORAMINES

Plant capacity, 10^6 l/day	Average water production, 10^6 l/day	Average capital cost, \$1,000	Annualized capital cost, \$1,000[a]	Average annual operating cost, \$1,000	Average total annualized cost, \$1,000
16	10	28	3	5	8
35	22	36	4	7	11
69	43	60	7	13	20
102	64	70	8	17	25
286	190	99	12	40	51
1,362	972	208	25	175	99

[a] Based on a 20-year life and 10 percent interest.

TABLE 12-4. CHLOROFORM REDUCTION POTENTIAL, COSTS, AND COST-EFFECTIVENESS BY USING CHLORAMINES

Average amount of water treated, 10^6 l/day	Average $CHCl_3$ produced prior to use of choramines, Mg/yr[a]	Average $CHCl_3$ produced after use of chloramines, Mg/yr[b]	$CHCl_3$ reduction potential, Mg/yr	Total annualized costs, \$1,000	Cost-effectiveness \$1,000/Mg
10	2.92×10^{-2}	2.92×10^{-3}	2.63×10^{-2}	8	304
22	6.42×10^{-2}	6.42×10^{-3}	5.78×10^{-2}	11	190
43	1.25×10^{-1}	1.25×10^{-2}	1.13×10^{-1}	20	177
64	1.87×10^{-1}	1.87×10^{-2}	1.68×10^{-1}	25	149
190	5.55×10^{-1}	5.55×10^{-2}	5.0×10^{-1}	51	102
972	2.84×10^{0}	2.84×10^{0}	2.56×10^{0}	99	38.7

[a] Based on an average $CHCl_3$ increase of 8 μg/l

[b] Based on an average $CHCl_3$ increase of 0.8 μg/l

The cost-effectiveness for using chloramines range from $304,000 per Mg for the smallest facility to $38,700 per Mg for the largest facility (Figure 12-1). Reductions in chloroform formation potential, costs, and cost-effectiveness are shown in Table 12-4.

Chlorine Dioxide--

Laboratory studies and use in drinking water treatment plants show that chlorine dioxide will disinfect without forming chloroform. Chlorine dioxide equipment can be retrofitted into water treatment plants. Existing chlorination equipment can be used as a standby. Because chlorine dioxide is unstable, it must be generated and used on-site. Reactor vessels are available from U.S. manufacturers, but the simplicity of design has encouraged several plants to fabricate their own.[8] In water treatment plants, chlorine dioxide is usually generated in reactors by three different methods: reacting chlorine gas and sodium chlorite; reacting sodium chlorite and a strong acid; or by mixing sodium hypochlorite, acid, and sodium chlorite. Small amounts of chlorine are carried over in chlorine dioxide production and form free chlorine in the water. However, a study has shown that even when the free chlorine concentration is half that of chlorine dioxide, chloroform formation is reduced by 90 percent.[9]

The design criteria for estimating the costs of using chlorine dioxide are: chlorine dioxide at a dose of 1 mg/l would replace chlorine as the disinfectant; a reaction vessel would be used to combine one part chlorine with one part sodium chlorite; and existing chlorination equipment would be modified to feed smaller amounts of chlorine, saving 1.5 mg of chlorine per liter.[4] The capital and operating costs for using chlorine dioxide are presented in Table 12-5. The total annualized costs range from $22,000 for the smallest plant to $997,000 for the largest plant.

The cost-effectiveness of using chlorine dioxide ranges from $608,000/Mg for the smallest facility to $370,000/Mg for the largest facility (Figure 12-1). Reductions in chloroform formation potential, costs, and cost effectiveness are shown in Table 12-6.

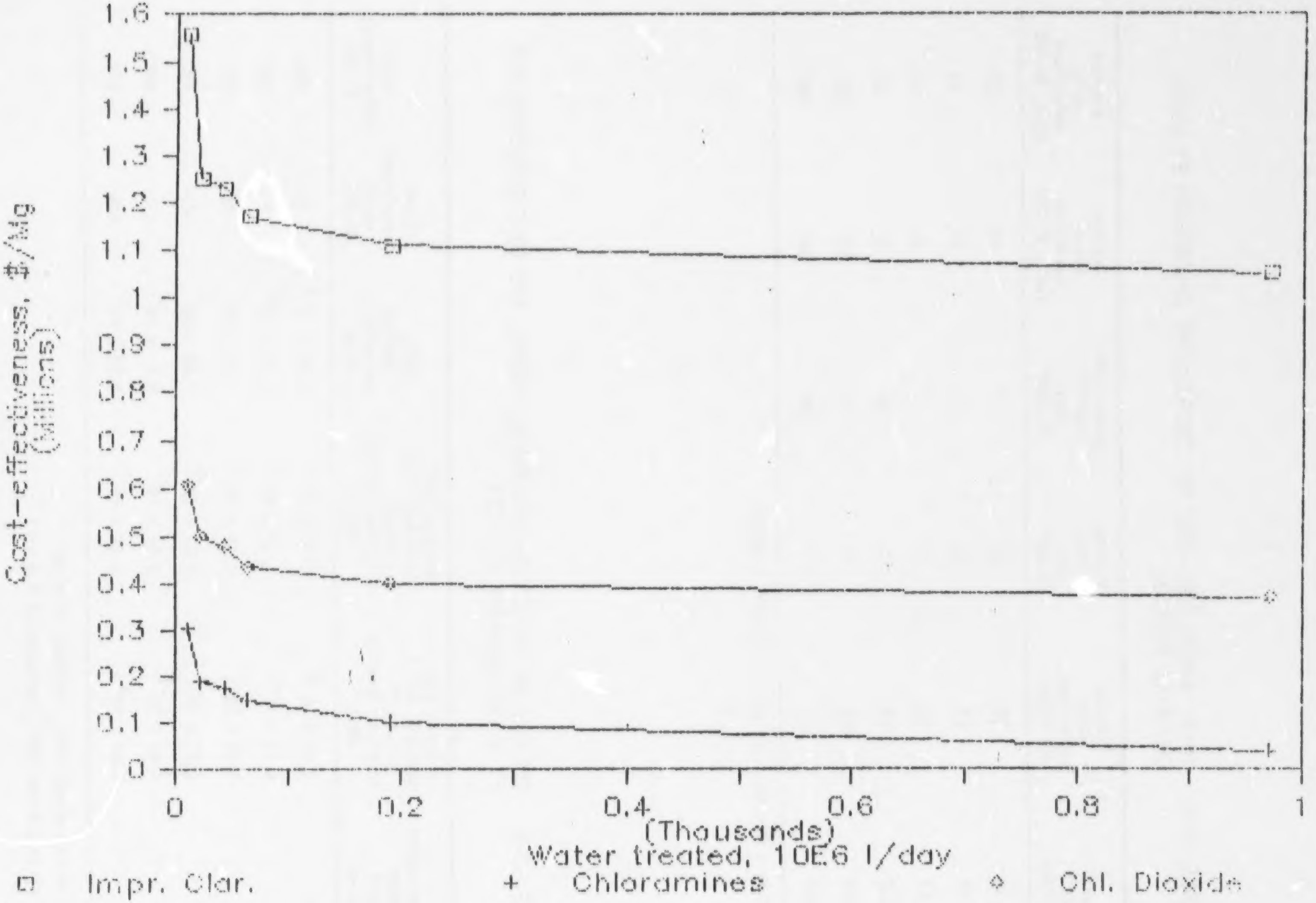

Figure 12-1. Cost-effectiveness of using improved clarification, chloramines, or chlorine dioxide during wastewater treatment.

TABLE 12-5. TOTAL ANNUALIZED COST OF CONTROLLING CHLOROFORM BY USING CHLORINE DIOXIDE

Plant capacity, 10^6 l/day	Average water production, 10^6 l/day	Average capital cost, $1,000	Annualized capital cost, $1,000[a]	Average annual operating cost, $1,000	Average total annualized cost, $1,000
16	10	47	6	16	22
35	22	55	6	29	35
69	43	63	7	54	61
102	64	120	14	73	87
286	190	174	20	201	221
1,362	972	420	49	948	997

[a] Based on a 20-year life and 10 percent interest

TABLE 12-6. CHLOROFORM REDUCTION POTENTIAL, COSTS, AND COST-EFFECTIVENESS BY USING CHLORINE DIOXIDE

Average amount of water treated, 10^6 l/day	Average $CHCl_3$ produced prior to use of chlorine dioxide Mg/yr[a]	Average $CHCl_3$ produced after use of chlorine dioxide, Mg/yr[b]	$CHCl_3$ reduction potential, Mg/yr	Total annualized costs, $1,000	Cost-effectiveness $1,000
10	2.92×10^{-2}	2.92×10^{-3}	2.63×10^{-2}	16	608
22	6.42×10^{-2}	6.42×10^{-3}	5.78×10^{-2}	29	502
43	1.25×10^{-1}	1.25×10^{-2}	1.13×10^{-1}	54	479
64	1.87×10^{-1}	1.87×10^{-2}	1.68×10^{-1}	73	435
190	5.55×10^{-1}	5.55×10^{-2}	5.0×10^{-1}	201	402
972	2.84×10^{0}	2.84×10^{-1}	2.56×10^{0}	948	370

[a] Based on an average $CHCl_3$ increase of 8 μg/l

[b] Based on an average $CHCl_3$ increase of 0.8 μg/l

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13. GRAIN FUMIGATION

INTRODUCTION

Chloroform is registered as a pesticide to control certain insects which commonly appear in stored, raw bulk grains. Vulcan Materials Company markets Chlorofume® FC 30 Grain Fumigant (Reg. No. 5382-15), which contains 72.2 percent chloroform, 20.4 percent carbon disulfide, and 7.4 percent ethylene dibromide.[1] Chlorofume® is produced as a ready-to-use fumigant. The end users primarily are small farm establishments which require inexpensive pesticide control. Chlorofume® provides this feature because it can be applied by one person. Some fumigants require physically turning the supply of stored grain, a labor intensive and thus costly operation.[1]

Chloroform as an ingredient in pesticides has been subject to considerable regulatory scrutiny in the last decade. Vulcan Materials Company originally obtained registration acceptance in 1968. In April 1976, the EPA issued a "Notice of Presumption Against Continued Registration of a Pesticide Product -- Chloroform (Trichloromethane)." The Notice was issued because of oncogenic effects in rats and mice as reported in a 1976 study by the National Cancer Institute. Continued study of chloroform ultimately resulted in returning it to the normal registration process.[2]

Recently there has been considerable debate on the use of ethylene dibromide (EDB) as a grain fumigant. On February 6, 1984 EPA cancelled registrations of pesticide products containing EDB (49 FR 4452). It is not known whether Vulcan plans to reformulate its product without EDB or not.

EMISSIONS

It is estimated that from 10,000 to 12,000 gallons per year of chloroform were used in grain fumigants from 1976 to 1979.[1] Vulcan reported sales of Chlorofume® (72.2 percent chloroform) of 7,000 gallons in 1981. This represents 5,054 gallons or 19,131 liters of chloroform. With a density of 1.48 kg/l, 28,400 kg or 28.4 Mg of chloroform were used in the application of grain fumigants. It is assumed that 100 percent of this volatilized during, and subsequent to, application. Thus 28.4 Mg of chloroform are emitted to air as a result of grain fumigation.

CONTROL TECHNIQUES

The only viable alternative for controlling releases of chloroform from grain fumigation would be to substitute another carrier such as carbon tetrachloride for chloroform. Carbon tetrachloride is used currently as a carrier in grain fumigation and is used in essentially all other fumigant mixtures. The best available estimates for average annual carbon tetrachloride use are 11,500 to 14,800 Mg between 1976 and 1979,[3] and 12,800 Mg for 1977 and 1978.[4] Thus, chloroform accounts for only 0.2 percent of the carriers used in grain fumigation, with carbon tetrachloride accounting for the remainder.

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